이학박사 학위논문

Efficient Metathesis Polymerizations Through Rational Design of Monomers: Cyclopolymerization of Diyne Derivatives Forming Small-to-Medium Rings and Ring-Opening Metathesis Polymerization of *cis*-Cyclooctenes

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Abstract

Olefin metathesis is a widely-used organic reaction to generate new carbon-carbon double bond by metal carbene . Above all, ring-opening metathesis polymerization (ROMP) is a representative chain growth metathesis polymerization for living polymerization. Cyclopolymerization (CP) is another chain-growth metathesis polymerization forming conjugated polyacetylene (PA) from diynes. To widely utilize cyclopolymerization generating PA derivatives having potential for organic electronics and optics, broader monomer scope and higher reactivity are required. This research describes the living/controlled CP of 1,7-octadiyne and 1,8-nonadiyne derivatives and Ring-Opening Metathesis Polymerization (ROMP) of *cis*-cyclooctenes through the rational design of monomers.

Chapter 2 describes the CP of N-containing 1,7-octadiyne derivatives using Grubbs catalyst. Introduction of hydrazide group having short C-N bond and enhanced Thorpe-Ingold effect enabled us to achieve living CP of 1,7-octadiynes.

Chapter 3 demonstrates the first CP of 1,8-nonadiyne derivatives using Grubbs catalyst. 1,8-nonadiyne was first utilized as a monomer for CP by

introduction of aminal and acetal groups. CP of 1,8-nonadiyne derivatives showed zeroth-order kinetics different from conventional polymerizations. Interestingly, we observed the active intermediate of olefin metathesis, 14e-Ru propagating carbene during CP.

Chapter 4 describes two strategies for controlled ROMP of *cis*-cyclooctenes. Although effect of bulky substituent was small for hindering chain transfer reaction, controlled ROMP of OTIPS-substituted cyclooctene was achieved.

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Chapter 1. Introduction

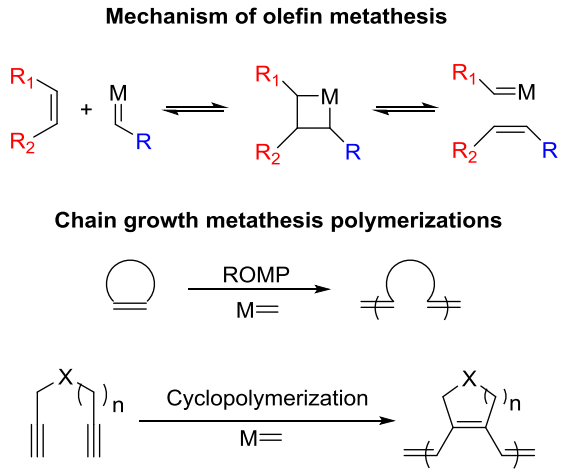
1.1 Research Background

Living olefin metathesis polymerizations

Living polymerization is a powerful tool to achieve a high degree of control over polymer chain architecture. The term 'living polymerization' was coined by Szwarc to describe that chain ends remain active in chain-growth polymerization until converted into an unreactive dead end by external factors such as addition of killing reagents. The more practical definition involves three features: i) narrow polydispersity index (PDI) lower than 1.5, ii) a linear relationship between the degree of polymerization (DP) and number-average molecular weight (M_n), and iii) continuous polymerization by further addition of monomer after consumption of monomer. To achieve living polymerization, no chain transfer and termination, and fast initiation (high k_i/k_p) are required. Various methods for living polymerization have been developed and enabled precise control of complex polymer structures including telechelic, graft, star, ladder and cyclic polymers, and block copolymers.

Olefin metathesis is a widely-used organic reaction to generate new carbon-carbon double bond by metal carbene (Scheme 1.1), but the first report on

olefin metathesis was the polymerization of bicycle[2.2.1]hept-2-ene (norbornene)[3]. With a development of well-defined catalyst and deep investigation on the mechanism by Schrock[4], Grubbs[5] and Feast[6], olefin metathesis polymerizations caused a drastic change in the field of synthetic polymer chemistry.[7] Above all, ring-opening metathesis polymerization (ROMP) is a representative chain growth metathesis polymerization for living polymerization (Scheme 1.1). Living ROMP enabled the synthesis of polymers with tunable sizes, shapes, and functions.[8] Cyclopolymerization (CP) is another chain-growth metathesis polymerization forming conjugated polyacetylene (PA) from diynes (Scheme 1.1). However, monomer for CP was limited to 1,6-heptadiyne over than twenty years due to challenging cyclization forming larger ring than six-membered ring.[9]

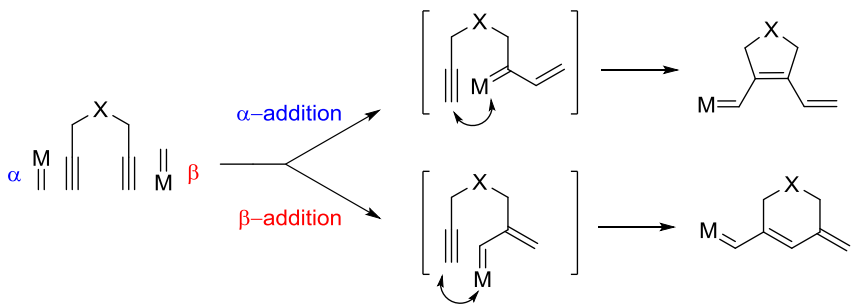


Scheme 1.1 Olefin metathesis and chain growth metathesis polymerization

Cyclopolymerization of diyne derivatives

CP of diyne derivatives using metal carbenes is a simple and powerful method for generating conjugated PAs containing cycloalkene repeat units. Conjugated PAs obtained by CP are stable in air and soluble in common organic solvents due to cycloalkane repeat units containing various side chains. Thus, the polymers have potential for use in organic electronics and optics.[10-12] As shown in Scheme 1.2, CP occurs through α- or β-addition depending on the orientation of the metal carbene binding to the terminal alkyne, resulting in the formation of five- and six-membered ring repeat unit, respectively. In the early development of CP, ill-defined catalysts such as Ziegler-Natta, $MoCl_5$, and WCl_6 catalysts were mainly employed to produce regio-random polyenes.[9] Then, development of well-defined alkylidene catalysts from the Schrock and Buchmeiser groups brought two important breakthroughs. Firstly, polymer microstructures and mechanisms based on α- or β-addition were thoroughly investigated using Schrock catalysts (Figure 1.1).[13] Furthermore, living CP via selective α- or β-addition produced well-defined conjugated polyenes containing either five- or six-membered rings.[14] The second important discovery came when the Buchmeiser group successfully achieved the CP forming five-membered rings

via exclusive α−addition employing user−friendly ruthenium catalysts by modifying air− and moisture−stable Hoveyda−Grubbs catalyst with electron−withdrawing groups (Figure 1.1).[14c,15]



Scheme 1.2 Regioselectivity for CP of 1,6−heptadyne

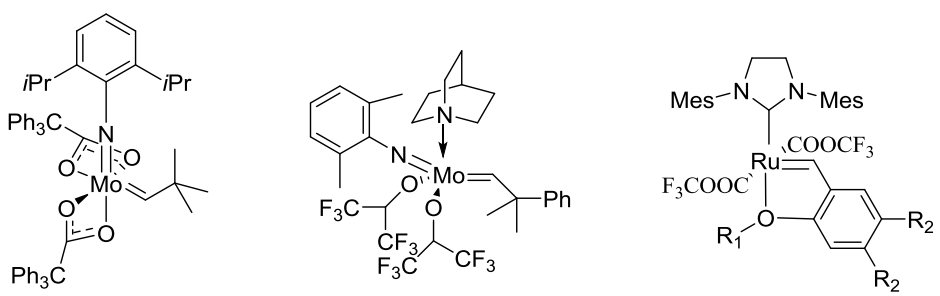


Figure 1.1 Mo−based Schrock catalysts and modified Ru−based Hoveyda−Grubbs catalysts promoting regioselective CP

Later, we reported the highly efficient living CP of 1,6−heptadiyne using a fast−initiating third−generation Grubbs catalyst[16] (**GIII**, Figure 1.2) both in THF and DCM.[17] Particularly in DCM, we discovered that lower reactivity in DCM was due to lower propagating carbene stability[17d] and competing

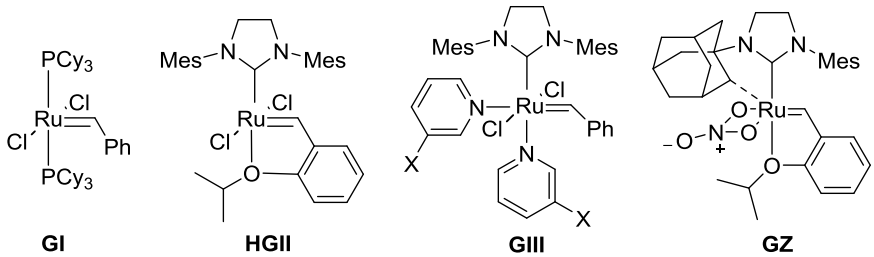
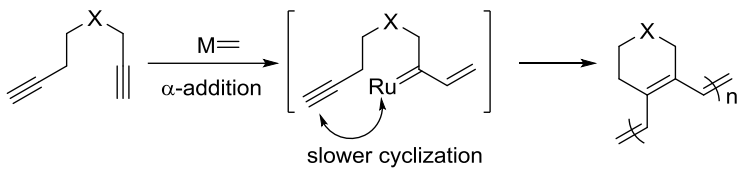


Figure 1.2 Ru-based Grubbs catalysts



Scheme 1.3 CP of 1,7-octadiyne via α-addition

[2+2+2] cycloaddition[18]. Living CP of 1,6-heptadiynes in DCM was achieved by the aid of 3,5-dichloropyridine stabilizing the propagating carbene.[17d] In addition, we expanded the utility of Ru-alkylidenes using a Grubbs *Z*-selective catalyst (**GZ**, Figure 1.2) to give conjugated polyenes containing six-membered rings[19] and a Grubbs 1st generation catalyst (**GI**, Figure 1.2) with benzoate additives[20]. To broaden monomer scope, various 1,7-octadiynes were designed to successfully generate new conjugated polyenes containing six-membered ring repeat units via α-addition of Ru and Mo catalysts (Scheme 1.3).[21] Although controlled CP of 1,7-octadiyne was achieved by **GIII**, slower polymerization rate was observed due to longer distance between

two alkynes compared to 1,6-heptadiynes.[21a] 1,8-nonadiyne derivative can be a monomer candidate for CP to generate new conjugated PAs containing seven-membered ring repeat unit via α-addition but, CP of 1,8-nonadiynes was not reported due to even longer distance between two alkynes.

1.2 Thesis Research

To widely utilize cyclopolymerization generating PA derivatives having potential for organic electronics and optics, broader monomer scope and higher reactivity are required. This research describes the living/controlled CP of 1,7-octadiyne and 1,8-nonadiyne derivatives and Ring-Opening Metathesis Polymerization (ROMP) of *cis*-cyclooctenes through the rational design of monomers.

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Chapter 4 describes two strategies for controlled ROMP of *cis*-cyclooctenes.

Although effect of bulky substituent was small for hindering chain transfer reaction, controlled ROMP of OTIPS-substituted cyclooctene was achieved.

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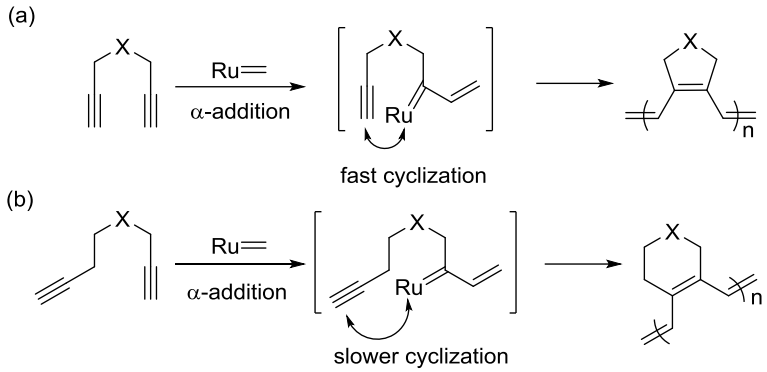
Chapter 2. Cyclopolymerization of N-Containing 1,7-Ocatdiyne Derivatives using Grubbs Catalysts

2.1 Abstract

Synthesis of a new class of conjugated polyenes containing N-heterocyclic six-membered rings was demonstrated via cyclopolymerization of N-containing 1,7-octadiyne derivatives using Grubbs catalysts. Successful cyclopolymerization was achieved by introducing protecting groups to the amines in the monomers. Moreover, a hydrazide-type monomer containing a di*tert*-butyloxycarbonyl group (**6**) promoted the living cyclopolymerization to give poly(**6**) with a controlled molecular weight and narrow dispersity. This living polymerization allowed us to prepare various conjugated diblock copolymers using poly(**6**) as the first block.

2.2 Introduction

Our group reported the first controlled cyclopolymerization (CP) of 1,7-octadiyne derivatives with Grubbs catalyst in which the α-addition produced six-membered ring repeat units selectively.[1a] However, we observed that the CP of the 1,7-octadiyne derivatives took long reaction time because the longer distance between the two alkynes resulted in a slower cyclization than that of 1,6-heptadiyne derivatives (Scheme 2.1). Our strategy to overcome this problem was enhancing the cyclization by a Thorpe-Ingold effect[2]. First, introduction of dimethyl substitution at the α-position of the side chain effectively accelerated the propagation of the 1,7-octadiyne derivatives.[1b] We also used 4,5-disubstituted 1,7-octadiynes instead of 4,4-disubstituted derivatives and higher reactivity was observed.[1c] Nevertheless, the cyclopolymerizations of these 1,7-octadiynes were still slow. Our next strategy to speed up the cyclization is to bring the two alkynes closer together by introducing a nitrogen atom because the C-N bond is shorter (1.47 Å) than the C-C bond (1.54 Å).



Scheme 2.1 Cyclopolymerization of 1,6-heptadiyne (a) and 1,7-octadiyne (b)

Among the previously reported nitrogen-containing diyne monomers, the CP of dipropargyl ammonium salts has been the most investigated.[3,4,5] There have also been several studies on the cyclopolymerizations of dipropargyl amine by $MoCl_5$, WCl_6[5] and Schrock-type catalysts[4a,c,6]. These previous studies on the CP of N-containing diynes had a selectivity issue which the addition mode is not controlled, thus the resulting polymers consisted of mixed five- and six-membered ring repeating units. Buchmeiser group broke through this limitation by introducing electron-withdrawing ligand in the Grubbs-type catalyst and achieved regioselective CP (α-addition only).[7] With this catalyst, they successfully synthesized the polyacetylenes which have ammonium- or amine-containing five-membered ring repeat units.[4d] However, this is the

only one example for the CP of amine-type monomers using Grubbs-type catalysts, because the strong coordination of free amines to the metal center tends to poison the catalysts[4c]. In particular, the CP of 1,7-octadiyne derivatives containing nitrogen has not been reported.

This section describes the successful cyclopolymerization of various 1,7-octadiyne derivatives containing a nitrogen at the 4-position or two nitrogens at the 4,5-positions with a proper choice of protecting groups. Furthermore, the living CP of 1,2-di*tert*-butyloxycarbonyl-1,2-dipropargyl hydrazine (**6**) was achieved.

2.3 Results and Discussion

The initial attempt to cyclopolymerize an amide-protected monomer **1** with third-generation Grubbs catalyst (Fig. 2.2, **GIII**)[8] gave the desired polymer in 65% yield in two hours (Table 2.1, entry 1). This was an improved result compared to the previous cyclopolymerization of a monosubstituted 1,7-octadiyne monomer (20% yield in 24 h).[1a] Several N-containing monomers with other protecting groups also underwent successful CP. The cyclopolymerizations of a sulfonamide-containing monomer **2** with 2 mol% **GIII** yielded the corresponding polymer in 75% yield in two hours. To further

improve the yield, the same polymerization of **2** was repeated with thermally stable second-generation Hoveyda-Grubbs catalyst (Fig. 2.2, **HGII**)[9] at 50 ℃, and the yield increased to 91% (Table 1, entry 2). **2** was the best monomer presumably because of the enhanced Thorpe-Ingold effect by the larger substituent. When the monomer feed ratio increased to 100, the polymer was produced in 64% yield (87% conversion, Table 2.1, entry 3). Carbamate-containing monomer **3** was also polymerized in high conversion of 85% (Table 2.1, entry 4) Poly(**4**), containing the less basic free aniline moiety, was also prepared in 63% yield (Table 2.1, entry 5). In short, these N-containing monosubstituted monomers seemed to be better monomers than the monosubstituted 1,7-octadiyne monomers.

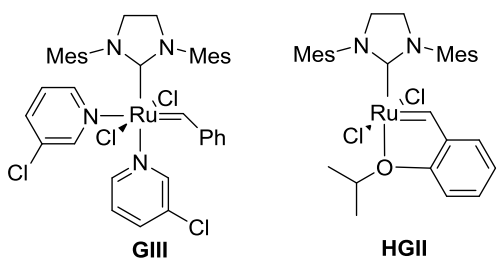
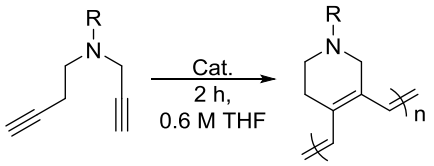
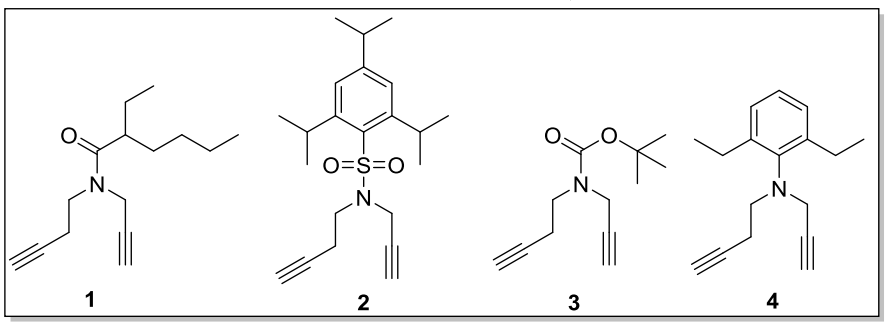


Figure 2.2 Structures of Grubbs catalysts

Table 2.1 Cyclopolymerization of monomers **1**–**4**





Entry	Monomer	Cat.	[M]/[I]	Temp (℃)	M_n (kDa)[a]	Đ [a]	Conv. (%)[b]	Yield (%)[c]
1	1	GIII	50	rt	11	2.36	76	65
2	2	HGII	50	50	19	2.14	99	91
3[d]	2	HGII	100	50	22	2.10	87	64
4	3	HGII	50	50	10	1.66	85	70
5	4	HGII	50	rt	8	1.60	79	63

[a] Determined by THF SEC calibrated using polystyrene (PS) standards. [b] Determined by crude ^{1}H–NMR. [c] Isolated yields after purification. [d] 1.2 M in THF.

To confirm the microstructure of the polymers, we independently synthesized the monomeric product containing a six-membered ring via enyne metathesis of **2** with ethylene. This model compound (**2'**) and poly(**2**) shared common chemical shifts in their ^{1}H and ^{13}C NMR spectra (5.15 ppm in ^{1}H NMR and 114.61 and 113.43 ppm in ^{13}C NMR, Figure 2.3). Other polymers showed similar peak patterns, confirming the regioselective CP via α-addition.

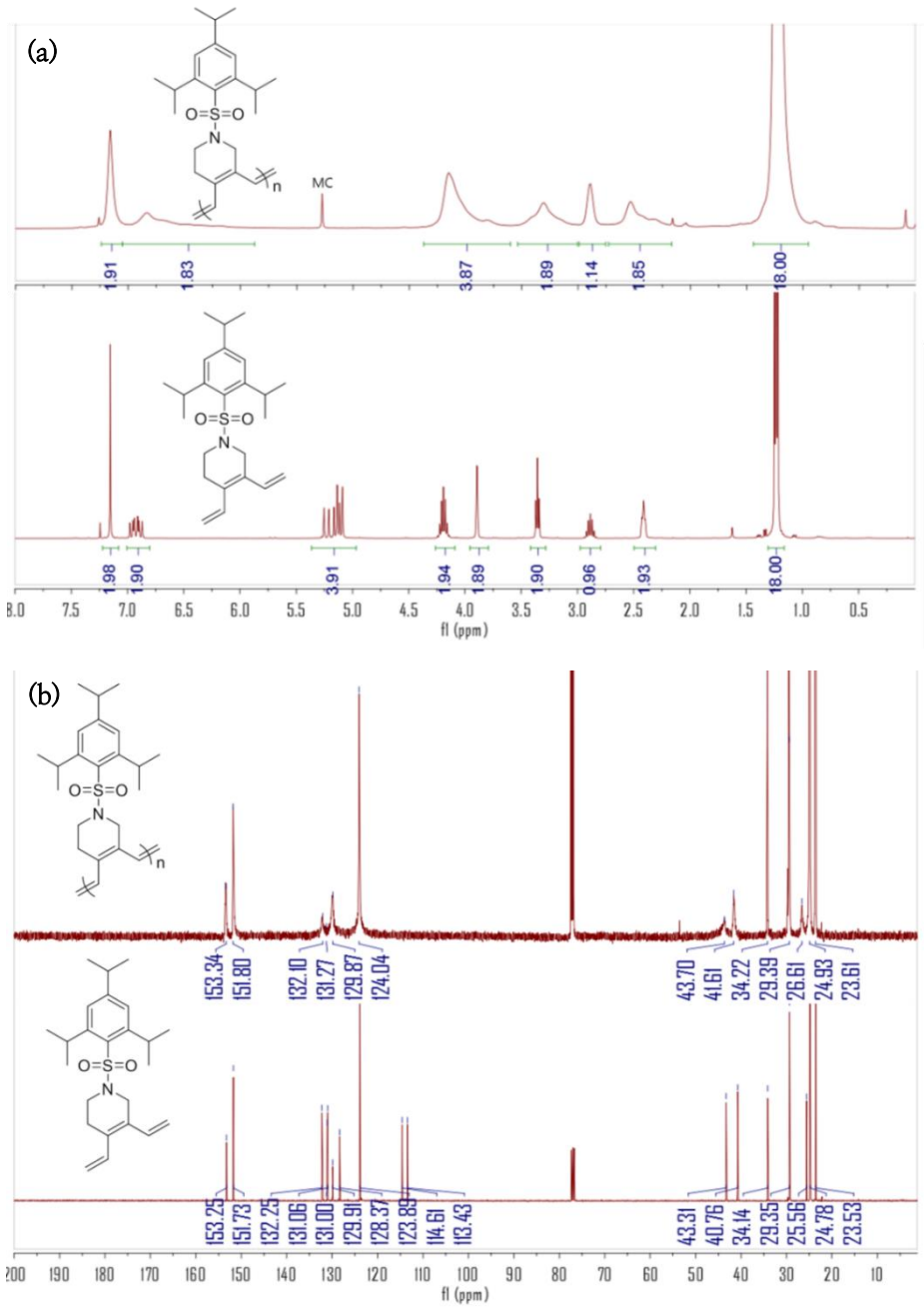


Figure 2.3 ^{1}H (a) and ^{13}C (b) NMR spectra of poly(**2**) and **2'**

In order to examine the origin of the improved reactivity of these nitrogen-containing monomers over the previous monosubstituted 1,7-octadiynes, we monitored the kinetics of the cyclopolymerization of a nitrogen and a carbon-containing 1,7-octadiyne derivative with the same substituent (**4a** and **4b**, Figure 2.4) in THF-d_8 by ^{1}H NMR to see if the carbamate group showed any positive effect on the propagation over the ester group. The initial reaction rate of **4a** (0.16 min^{-1}) was relatively faster than that of **4b** containing the ester (0.12 min^{-1}), presumably because of shorter C-N bond length. Furthermore, the conversion of **4a** showed a steady increase over time, whereas no further conversion of **4b** was observed after eight minutes. This result implied that the lifetime of the propagating carbene was longer for **4a** than **4b**, presumably because the more electron-rich carbonyl group on the carbamate of **4a** stabilized the propagating carbenes more effectively than the ester carbonyl in **4b**.[10a,b] In short, the origins of the improved cyclopolymerization of **4a** over **4b** seemed to be the shorter distance between the two alkynes on **4a** and the longer lifetime of the propagating carbene. However, it seemed impossible to further increase the reactivity of these N-containing monomers with only a single substituent because of the lack of the Thorpe-Ingold effect.

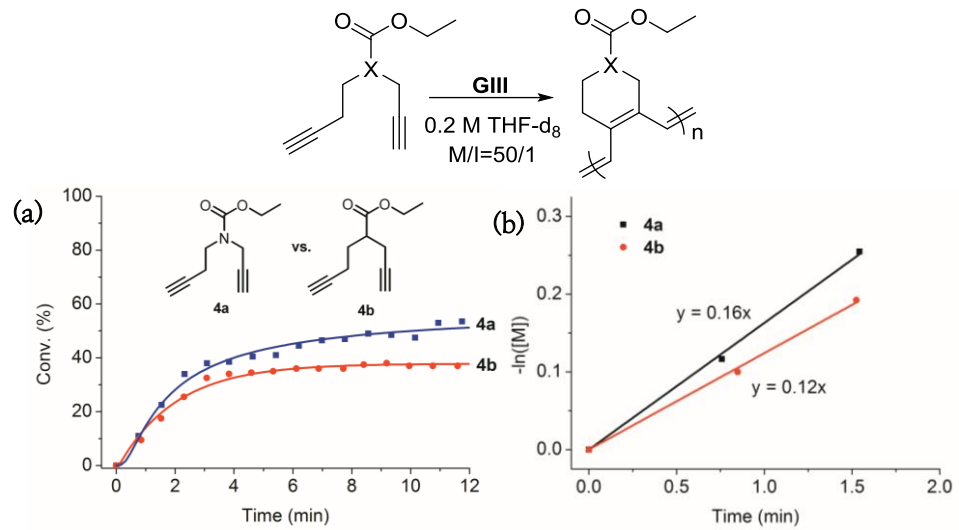
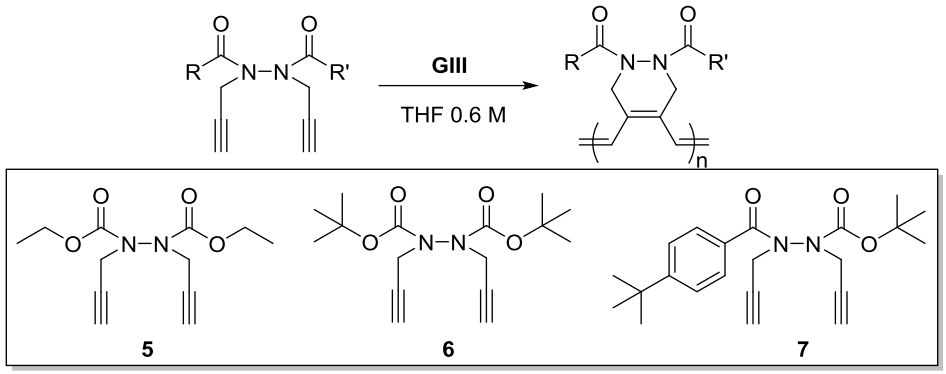


Figure 2.4 Plot of conversion (a) and −ln[M] (b) over time during the CP of **4a** and **4b**

To further enhance the reactivity of the cyclopolymerization of 1,7-octadiyne derivatives, we introduced two nitrogen atoms as bis-protected hydrazines (Table 2.2). By using 2 mol% **GIII**, the cyclopolymerization of the hydrazide-type monomers was greatly accelerated compared to that of the previous monomers containing a single protected nitrogen (Table 2.2). Firstly, the cyclopolymerization of **5**, containing diethoxycarbonyl hydrazine, was complete within 15 min, but the molar-mass dispersity (Đ) was slightly broad (1.42), presumably because of the occurrence of some chain-transfer reaction (Table 2.2, entry 1). To suppress the chain-transfer reaction, we designed a new monomer **6** with the bulkier di*tert*-butyloxycarbonyl (*t*-BOC) group; **6**

Table 2.2 Cyclopolymerization of monomers 5–7



Entry	Monomer	[M]/[I]	Temp (℃)	Time (min)	M_n (kDa)[a]	Đ[a]	Yield (%)[b]
1	5	50	rt	15	18	1.42	88
2	6	50	rt	5	16	1.16	90
3	7	50	rt	30	14	1.44	95
4	6	25	10	30	9	1.12	88
5	6	50	10	30	18	1.18	95
6	6	75	10	60	27	1.25	95
7	6	100	10	90	37	1.39	94

[a] Determined by chloroform SEC calibrated using polystyrene (PS) standards. [b] Isolated yields after purification. All the monomers were converted to polymer.

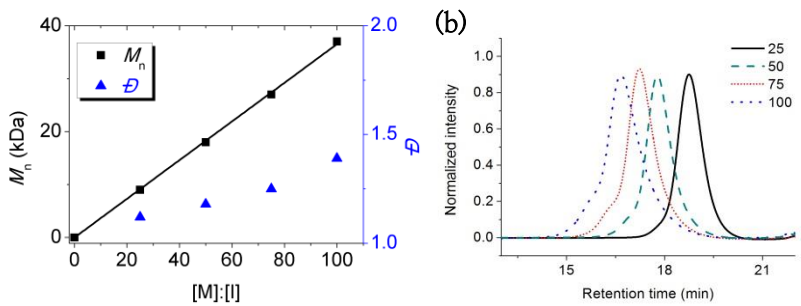


Figure 2.5. Correlation between M_n over [M]:[I] (a) and their SEC traces (b) for poly(6)

was completely converted within 5 min to give a polymer with a dispersity of 1.16 (Table 2.2, entry 2). This improved reactivity was comparable to that of 1,6-heptadiyne derivatives with catalyst **GIII**.[10a] When one of *t*-BOC groups in **6** was changed to the smaller *para-tert*-butylbenzoyl group (**7**), the reaction was complete within 30 min (Table 2.2, entry 3). Even though the reaction was slower than with **5**, it still maintained a faster rate than the previous monomers containing single nitrogen. To check the possibility of living polymerization of **6**, the polymerization temperature was lowered to 10 ℃ as the optimized conditions[11], and we found that the molecular weights of poly(**6**) were directly proportional to the [M]:[I] ratio; excellent control over the [M]:[I] from 25:1 to 100:1 and narrow dispersities were maintained (Table 2.2, entries 4 – 7 and Figure 2.5).

The microstructure of these polymers containing six-membered rings as repeat units was confirmed by ^{13}C NMR analysis in the same way as the previous monosubstituted amine-type polymers (Figure 2.6). The model compound **6'** and poly(**6**) shared common chemical shifts in their ^{1}H and ^{13}C NMR spectra except the terminal olefin signals in **6'** (4.91 ppm in ^{1}H NMR and 113.93 ppm in ^{13}C NMR). For exact analysis, NMR was taken in benzene-d_6 at 60 ℃ due to the splitting by rotational isomer.

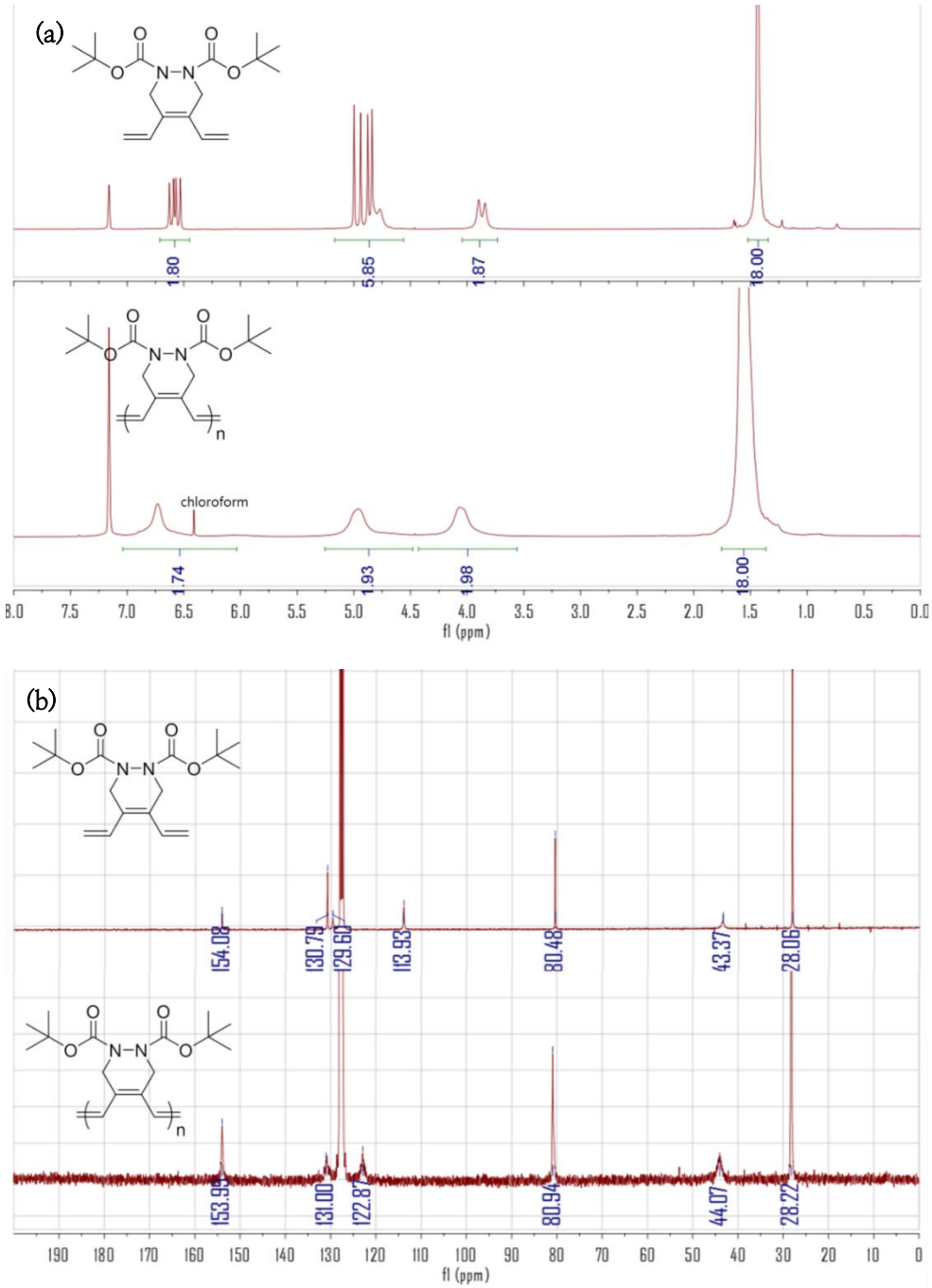


Figure 2.6 ^{1}H (a) and ^{13}C (b) NMR spectra of poly(**6**) and **6'**

To confirm whether the origin of improved reactivity of hydrazide-type monomers comes from short bond length of N-N or enhanced Thorpe-Ingold effect, we compared the kinetics for CP of **5** and its carbon derivative (**5'**). Interestingly, consumption of carbon monomer **5'** was faster than **5**. This presumably resulted from high rotational barrier of N-N bond in diacylhydrazines (E_a = ~19 kcal/mol)[14]. The rotameric broad signals observed in ^{1}H and ^{13}C NMR support this explanation. Although the reactivity of hydrazide monomer was lower than its carbon derivative, we concluded that the origin of improved reactivity of hydrazide-type monomer was enhanced Thorpe-Ingold effect by introduction of two substituents.

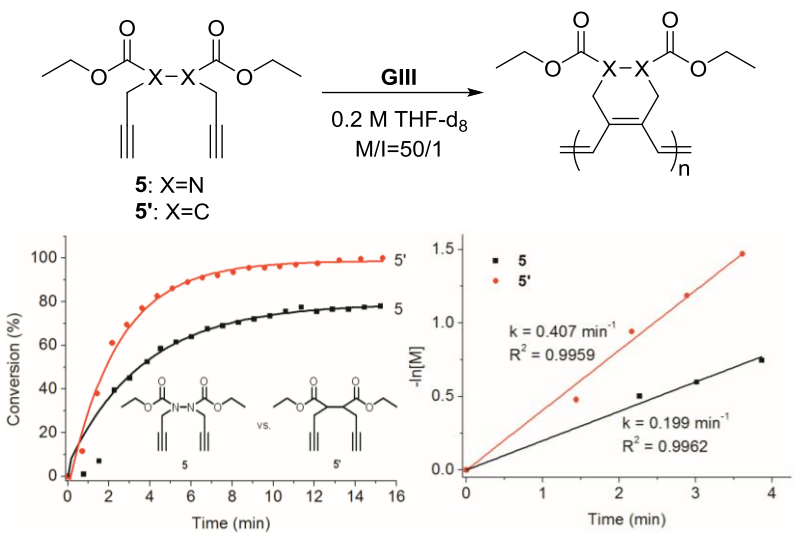
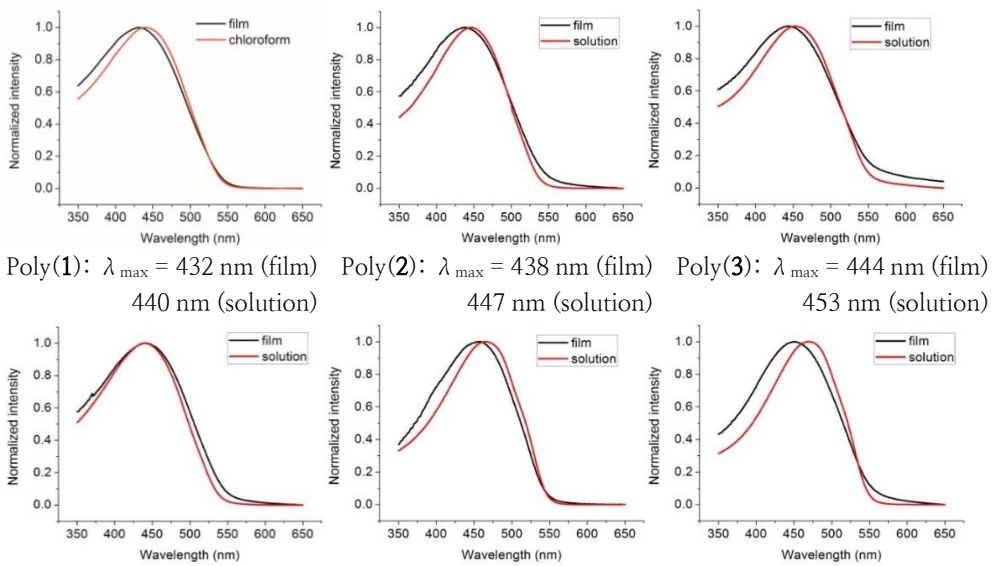


Figure 2.7 Plot of conversion over time during the CP of **5** and **5'**

These conjugated polymers containing six-membered N-heterocyclic repeat units were analyzed by UV-Vis spectroscopy. Their band gaps were approximately 2.3 eV with an onset around 550 nm, and λ_{max} in chloroform was in the range of 440 – 450 nm for the polymers containing mono-substituted amines and 440 – 475 nm for the bis-substituted hydrazide-type polymers (Figure 2.7). The lower λ_{max} values in comparison to those of poly(dipropargylamines) with five-membered ring structures (480 – 600 nm)[4d] suggested that the new polymers with six-membered N-heterocyclic structures adapted a less coplanar polymer conformation, resulting in a shorter conjugation length.



Poly(**1**): λ_{max} = 432 nm (film) 440 nm (solution) Poly(**2**): λ_{max} = 438 nm (film) 447 nm (solution) Poly(**3**): λ_{max} = 444 nm (film) 453 nm (solution)

Poly(**5**): λ_{max} = 442 nm (film) 440 nm (solution) Poly(**6**): λ_{max} = 456 nm (film) 467 nm (solution) Poly(**7**): λ_{max} = 452 nm (film) 469 nm (solution)

Figure 2.7 UV-vis spectra of poly(**1**)-poly(**7**)

The initial *cis*/*trans* ratio for poly(**6**) was 1/13, calculated by ^{1}H NMR. After 5 h of blue LED irradiation in THF-d_8, isomerization occurred, as confirmed by disappearance of the signal for the *cis*-olefin (Figure 2.9).[12] Furthermore, this isomerized poly(**6**) showed an increased λ_{max} from 467 to 482 nm because of the extended conjugation length as a result of the higher *trans*-olefin ratio (Figure 2.8a). To confirm that nitrogen atom affects the polymer backbone, we observed the change of UV/vis spectra of poly(**5**) and poly(**5'**) during isomerization under blue LED. Initial λ_{max} for poly(**5'**) (461 nm) was larger than that for poly(**5**). However, after isomerization, larger λ_{max} for poly(**5**) (485 nm) was observed (Figure 2.8b and 8c), implying that nitrogen-containing conjugated polymer had longer effective conjugation length than its carbon derivative. Furthermore, after irradiation for 38 h, backbone of poly(**5'**) decomposed whereas, poly(**5**) remained stable. In short, nitrogen had a positive effect on the stability and conjugation length.

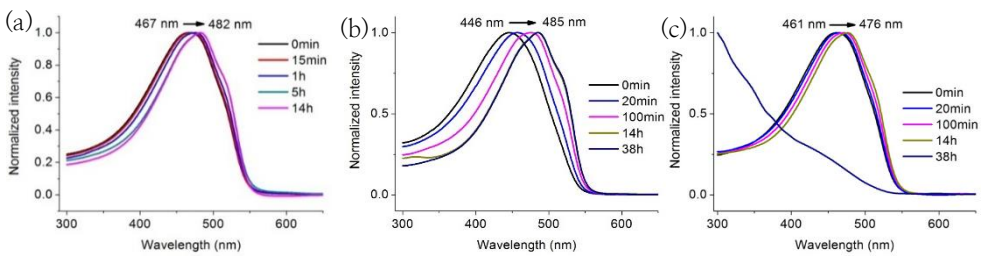


Figure 2.8 Change of UV-vis spectra during isomerization of (a) poly(**6**) (b) poly(**5**) and (c) poly (**5'**)

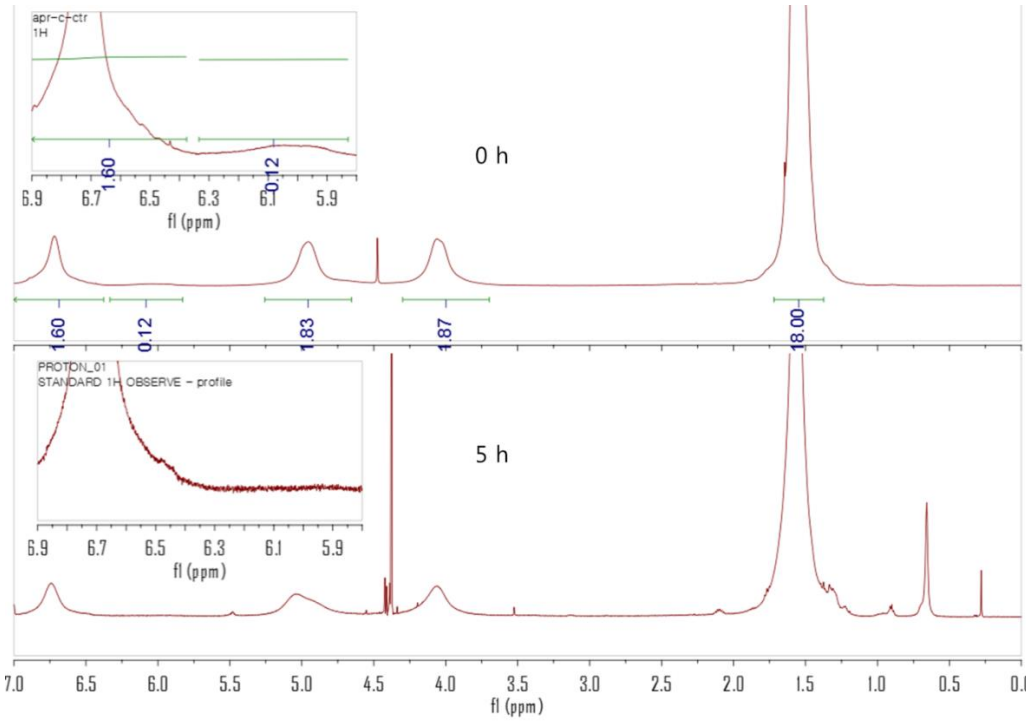


Figure 2.9 ^{1}H NMR spectra of before- and after-isomerization of poly(**6**)

Living cyclopolymerization provides a convenient method to prepare various conjugated block copolymers.[10a,13] Previously, 1,7-octadiyne derivatives were only used as the second monomer for block copolymerization using a Grubbs catalyst because of their relatively low reactivity[1a,b]; when 1,7-octadiyne derivatives were used for the first block, the final block copolymers were always contaminated by small amounts of their homopolymers.[1c] However, various diblock copolymers could be prepared with the highly reactive poly(**6**) as the first block (Figure 2.10). The block copolymerization of **6** and **7** with **GIII** produced, for the first time, a block copolymer consisting of two different six-membered heterocycles. Furthermore, block copolymerizations of **6** and 1,6-heptadiyne **8** produced diblock copolymer poly(**6**)-*b*-poly(**8**) containing blocks of six-membered heterocycle and five-membered carbocycle repeat units. Lastly, a 4,5-disubstituted 1,7-octadiyne monomer[1c] was used as a second block to give poly(**6**)-*b*-poly(**9**) containing blocks of six-membered heterocycle and six-membered carbocycle repeat units. The microstructures of these block copolymers were verified by size-exclusion chromatography (SEC), which showed the complete shifts of the traces from the initial poly(**6**) to higher molecular weight regions (Figure 2.10, (b) – (d)) while maintaining their narrow dispersities (Figure 2.10).

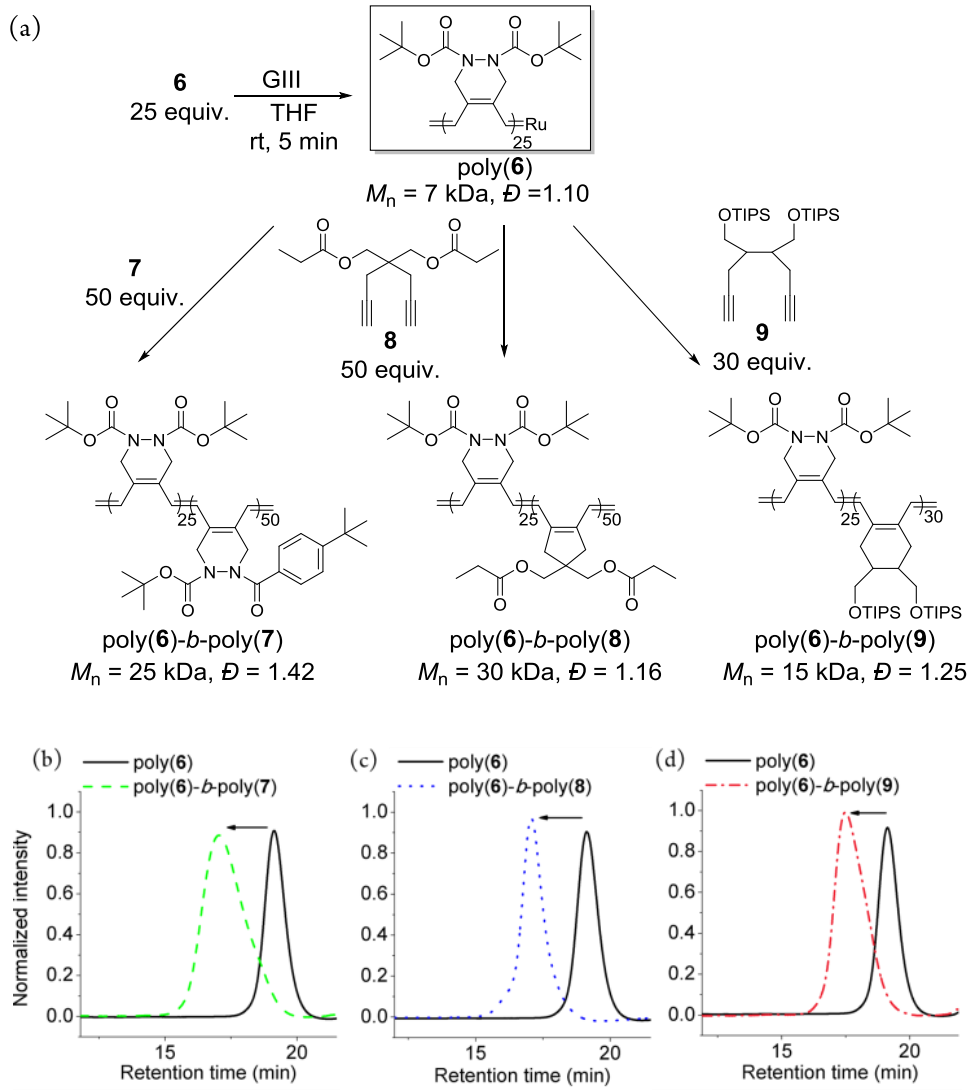


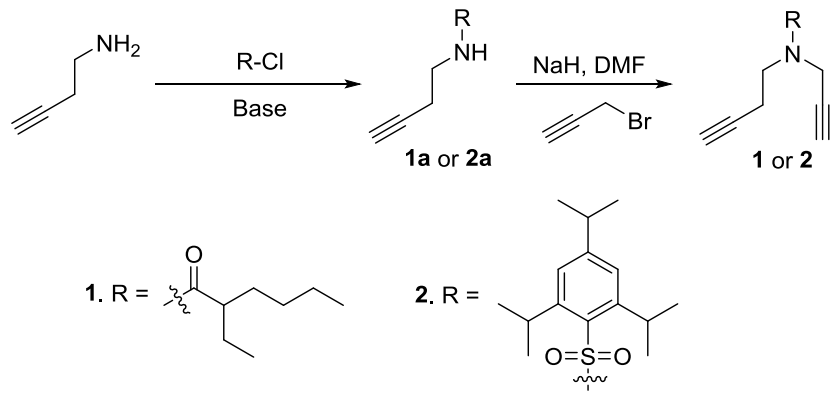
Figure 2.10 (a) Diblock copolymerization of 6 and various diyne derivatves. SEC traces of homopolymer poly(**6**) and diblock copolymers: (b) poly(**6**)-*b*-poly(**7**), (c) poly(**6**)-*b*-poly(**8**), and (d) poly(**6**)-*b*-poly(**9**)

2.4 Conclusion

We demonstrated the synthesis of new conjugated polymers consisting of various six-membered N- or N,N'-heterocyclic repeat units via regioselective cyclopolymerization of nitrogen-containing 1,7-octadiyne derivatives. Introducing protecting groups and bulky substituents led to improved cyclopolymerization results compared to those observed in the case of the corresponding all-carbon monomers. Using ^{1}H NMR kinetic studies, we concluded that the N-containing monomers gave higher conversion because of the shorter C-N bond length and the stabilizing effect on the propagating carbene. By introducing the hydrazide group, the reactivity increased greatly, and we could achieve the living cyclopolymerization of monomer **6** to produce conjugated polymers with controlled molecular weights and narrow dispersities. This living polymerization allowed the synthesis of various diblock copolymers with poly(**6**) as the first block, and this expanded the monomer scope for block copolymerization. This work demonstrates that the introduction of a heteroatom effectively increased the reactivity and utility of the cyclopolymerization.

2.5 Experimental Section

Monomer **5'**[1c], **6**[16], **8**[10a] and **9**[1c] were synthesized according to the procedure reported in the literature.



Scheme S1. Synthesis of Monomers **1** and **2**

1a: 1-Amino-3-butyne (4 mmol, 276.4 mg) was added to the Ar-purged flask in DCM (16 ml). TEA (4.2 mmol, 0.59 ml) and 2-ethylhexanoyl chloride (4.2 mmol, 683.2 mg) were added to the reaction mixture and the mixture was stirred for 1 h. The reaction mixture was quenched with NH_4Cl solution. Product was extracted with diehyl ether and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane = 1:5) to afford compound **1a**

as a white solid (664.0 mg, 85 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.87 (6H, dd, J = 14.4, 7.4 Hz, $(CH_2)_4CH_3$ and CH_2CH_3), 1.26 (4H, m, $CH_2(CH_2)_2CH_2$), 1.42 (2H, m, $(CH_2)_3CH_2CH_3$), 1.91 (1H, m, $CHCH_2CH_3$) 1.98 (1H, t, J = 2.6 Hz, CCH), 2.40 (2H, dt, J = 6.32, 2.6 Hz, CH_2CH_2C), 3.41(2H, dd, J = 12.44, 624 Hz, NCH_2), 5.73 (1H, s, NH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 12.07, 13.95, 19.54, 22.72, 26.05, 29.80, 32.49, 37.71, 49.80, 69.80, 69.84, 76.65, 76.97, 77.17, 77.29, 81.67; IR: 3310, 2960, 2933, 1648, 1545, 1268, 1232, 740, 703, 633 cm^{-1}; HRMS (EI+): calcd. for $C_{12}H_{21}ON$, 195.1623, found, 195.1618.

1: **1a** (3 mmol, 585.9 mg) was added to the Ar-purged flask in DMF (18 ml). Solution was cooled to 0 ℃ and sodium hydride (3.5 mmol, 84 mg) was added. After stirring for 15 min at room temperature, propargyl bromide in toluene solution (3.5 mmol, 0.26 ml) was added to the reaction mixture. After 12 h at 80 ℃, the mixture was quenched by aqueous NH_4Cl aqueous solution. Product was extracted with ethyl acetate and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane = 1:20) to afford compound **1** as a colorless liquid (140.0 mg,20 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.86 (6H, dd, J = 10.88,

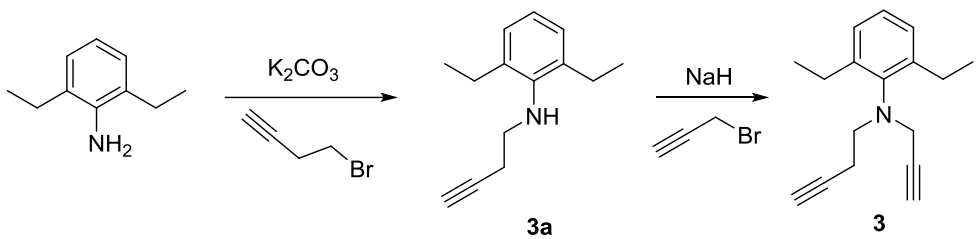
5.04 Hz, $(CH_2)_4CH_3$ and CH_2CH_3), 1.24 (4H, m, $(CH_2)_2CH_2CH_3$), 1.46 (2H, m, $(CH_2)_3CH_2CH_3$) 1.63 (2H, m, $CHCH_2CH_3$), 1.98 (1H, d, J = 33.8 Hz, CC*H*), 2.23 (1H, d, J = 37.84. Hz, CC*H*), 2.49 (2H, m, CH_2CH_2C), 2.57 (1H, m, COC*H*), 3.56 (1H, m, NCH_2CH_2, rotamer), 3.65 (1H, t, J = 5.92 Hz, NCH_2CH_2, rotamer), 4.20 (1H, s, NCH_2C, rotamer), 4.26 (1H, dd, J = Hz, 18.8, 4.76 Hz, NCH_2C, rotamer); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 11.91, 13.90, 17.64, 19.16, 22.83, 22.90, 25.99, 26.02, 29.67, 29.71, 32.46, 32.52, 34.51, 38.58, 42.88, 43.07, 45.48, 45.55, 69.57, 70.72, 71.60, 72.38, 79.02, 79.23, 80.28, 81.87, 176.50; IR: 3306, 2960, 2931, 1643, 1464, 1425, 1266, 1199, 1172, 1054, 741, 703, 640 cm^{-1}; HRMS (FAB+): calcd. for $C_{15}H_{24}NO$, 234.1858, found, 234.1854.

2a: 1-Amino-3-butyne (1 mmol, 69.11 mg) was added to the Ar-purged flask in DCM (6 ml). TEA (1.5 mmol, 0.2 ml) and 2,4,6-triisopropylbenzenesulfonyl chloride (1.2 mmol, 363.4 mg) were added to the reaction mixture and the mixture was stirred for 12 h. The reaction mixture was quenched with NH_4Cl solution. Product was extracted with diethyl ether and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane =1:10) to afford

compound **2-1** as a white solid (318.7 mg, 95 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.23 (18H, m, CH(C*H*$_3$)$_2$), 1.95 (1H, t, *J* = 2.64 Hz, CC*H*), 2.38 (2H, td, *J* = 6.64, 2.64 Hz, C*H*$_2$C), 2.87 (1H, qui, *J* = 6.92 Hz, C*H*(CH$_3$)$_2$), 3.10 (2H, dd, *J* = 13.20, 6.60 Hz, NHC*H*$_2$), 4.13 (2H, m, C*H*(CH$_3$)$_2$), 4.96 (1H, t, *J* = 6.48 Hz, N*H*); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 19.75, 23.54, 24.87, 29.60, 34.08, 41.26, 70.87, 80.49, 123.80, 132.16, 150.25, 152.77; IR: 3309, 2959, 2870, 1600, 1562, 1425, 1363, 1320, 1150, 1083, 882, 749, 656 cm^{-1}. HRMS (EI+): calcd. for $C_{19}H_{29}NO_2S$, 335.1919, found, 335.1921.

2: **2a** (1 mmol, 373.56 mg) was added to the Ar-purged flask in DMF (6 ml). Solution was cooled to 0 ℃ and sodium hydride (1.2 mmol, 28.8 mg) was added. After stirring for 15 min at room temperature, propargyl bromide in toluene solution (1.5 mmol, 0.11 ml) was added to the reaction mixture. After 2 h, the mixture was quenched by aqueous sodium bicarbonate solution. Product was extracted with ethyl acetate and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane =1:20) to afford **2** as the pale yellow solid (343.67 mg, 92 %). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.27 (18H, d, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.99 (1H, t, *J* = 2.65 Hz, CC*H*), 2.30 (1H, t, *J* = 2.45 Hz, CC*H*),

2.54 (2H, td, J = 7.6, 2.75 Hz, NCH_2CH_2C), 2.91 (1H, sept, J = 6.95 Hz, $CH(CH_3)_2$), 3.55 (2H, t, J = 7.4 Hz, NCH_2CH_2), 4.07 (2H, d, J = 2.5 Hz, NCH_2C), 4.10 (2H, sept, J = 6.80 Hz, $CH(CH_3)_2$), 7.18 (2H, s, Ar); ^{13}C-NMR (125MHz, $CDCl_3$): δ 17.82, 23.45, 24.73, 29.35, 33.90, 35.67, 44.30, 70.59, 74.39, 80.87, 124.44, 130.25, 151.73, 153.55; IR: 3294, 2960, 2870, 1600, 1318, 1152, 745, 664 cm^{-1}; HRMS (FAB+): calcd. for $C_{22}H_{32}NO_2S$, 374.2154, found, 374.2149.



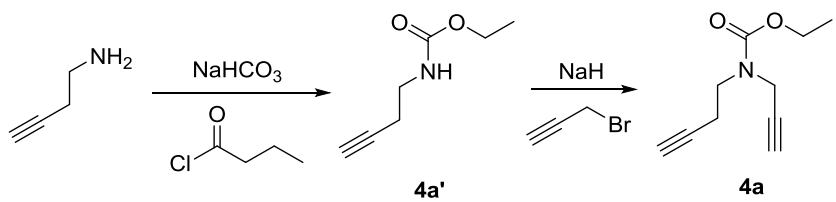
Scheme S2. Synthesis of Monomers 3

3a: 2,6-diethyl aniline (4 mmol, 596.8 mg) was added to the Ar-purged flask in DMF (24 ml). K_2CO_3 (4.2 mmol, 580.3 mg) and 4-bromo-1-butyne (4.1 mmol, 545.3 mg) were added to the solution. After 12 h at 85 ℃, the mixture was quenched by aqueous NH_4Cl solution. Product was extracted with ethyl acetate and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane = 1:20) to

afford the pale yellow solid (**3-1**, 217.4 mg, 27 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.25 (6H, m, CH_2CH_3), 2.08, (1H, s, CC*H*), 2.48 (2H, s, $NHCH_2C$), 2.69 (4H, dd, J = 15.08, 7.04 Hz, CH_2CH_3), 3.09 (2H, s, $NHCH_2CH_2$), 3.40 (1H, s, NH), 6.97 (1H, d, *J* = 6.20 Hz, Ar), 7.04 (2H, s, Ar); ^{13}C-NMR (100MHz, $CDCl_3$): δ 14.89, 20.30, 24.49, 48.15, 69.97, 82.27, 122.99, 126.64, 136.68, 144.18; IR: 3305, 2965, 2934, 2873, 1456, 1260, 1197, 753, 641 cm^{-1}; HRMS (EI+): calcd. for $C_{14}H_{19}N$, 201.1517, found, 201.1523.

3: **3a** (201.3 mg, 1 mmol) was added to the Ar-purged flask in DMF (6 ml). Solution was cooled to 0 ℃ and sodium hydride (1.2 mmol, 28.8 mg) was added. After stirring for 15 min at room temperature, propargyl bromide in toluene solution (1.5 mmol, 0.11 ml) was added to the reaction mixture. After 12 h at 95 ℃, the mixture was quenched by aqueous NH_4Cl solution. Product was extracted with ethyl acetate and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane =1:30) to afford the colorless liquid (**3**, 201.1 mg, 84 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.24 (6H, m, CH_2CH_3), 1.94 (1H, s, CC*H*), 2.24 (1H, s, CC*H*), 2.41 (2H, m, CH_2CH_2C), 2.72 (4H, dd, *J* = 15.08 7.56

Hz, CH_2CH$_3$), 3.38 (2H, t, J = 7.92 Hz, NCH_2CH$_2$), 3.85 (2H, s, NCH_2C), 7.09 (3H, m, Ar); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 15.40, 19.57, 24.55, 43.89, 53.16, 69.08, 71.81, 81.45, 82.75, 126.34, 126.67, 143.91, 146.14; IR: 3301, 2965, 2932, 2873, 1457, 1191, 770, 633 cm^{-1}; HRMS (EI+): calcd. for $C_{17}H_{21}N$, 239.1674, found, 239. 1676.



Scheme S3. Synthesis of Monomers **4a**

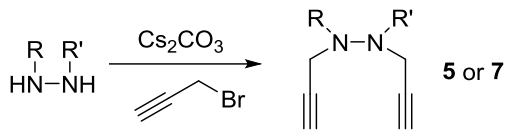
4a': 1-Amino-3-butyne (4 mmol, 276.4 mg) was added to the Ar-purged flask in ethanol (16 ml). $NaHCO_3$ (4.2 mmol, 352.8 mg) and ethyl chloroformate (4.2 mmol, 0.4 ml) were added to the reaction mixture and the mixture was stirred for 1 h. The reaction mixture was quenched with NH_4Cl solution. Product was extracted with diehyl ether and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane = 1:10) to afford compound **4a'** as a colorless liquid (536.4 mg, 95 %). ^{1}H-NMR (500 MHz, $CDCl_3$): δ

1.20 (3H, t, J = 7.05 Hz, CH_2CH_3), 1.98 (1H, t, J = 2.65 Hz, CCH), 2.36 (2H, td, J = 6.50, 2.55 Hz, CH_2CH_2C), 3.29 (2H, dd, J = 12.65, 6.30 Hz, NHCH_2), 4.07 (2H, dd J = 14.05, 7.05 Hz, OCH_2), 5.14 (1H, s, NH); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 14.33, 19.84, 39.54, 59.85, 70.25, 81.55, 156.49; IR: 3300, 2982, 1965, 1528, 1251, 1073, 1033, 779, 638 cm^{-1}; HRMS (FAB+): calcd. for $C_7H_{12}NO_2$, 142.0868, found, 142.0867.

4a: 4a' (141.2 mg, 1 mmol) was added to the Ar-purged flask in DMF (6 ml). Solution was cooled to 0 ℃ and sodium hydride (1.2 mmol, 28.8 mg) was added. After stirring for 15 min at room temperature, propargyl bromide in toluene solution (1.5 mmol, 0.11 ml) was added to the reaction mixture. After 1 h, the mixture was quenched by aqueous NH_4Cl solution. Product was extracted with ethyl acetate and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane =1:20) to afford the colorless liquid (134.4 mg, 75 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.24 (3H, t, J = 7.12 Hz, CH_2CH_3), 1.95 (1H, t, J = 2.56 Hz, CCH), 2.21 (1H, t, J = 2.44 Hz, CCH), 2.46 (2H, s, CH_2CH_2C), 3.50 (2H, t, J = 7.12 Hz, NCH_2CH_2), 4.13 (4H, m, NCH_2C and OCH_2); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.56, 18.31, 36.89, 45.05, 45.73, 61.80, 69.78,

71.98, 79.11, 81.26, 155.70; IR: 3296, 2982, 1699, 1419, 1246, 1123, 750, 646 cm^{-1}; HRMS (EI+): calcd. for $C_7H_{15}O_5$, 179.0946, found, 179.0949.

4b: 2-(3-butyn-1-yl)-2-(2-propyn-1-yl)-1,3-diethyl ester[6(c)] (2 mmol, 356.5 mg) was added to the flask in DMSO (12 ml). LiCl (4 mmol, 169.6 mg) and H_2O (0.12 ml) were added to the solution. The mixture was refluxed for 5 h under air. The product was extracted with diethyl ether and the organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane = 1:20) to afford compound **4b** as a colorless liquid (292.3 mg, 82 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.22 (3H, t, J = 16 Hz, CH_2CH_3), 1.84 (2H, m, $CHCH_2CH_2$), 1.92 (1H, t, J = 4 Hz, CCH), 1.95 (1H, t, J = 4 Hz, CCH), 2.19 (2H, m, CH_2CH_2C), 2.41 (2H, m, $CHCH_2C$), 2.66 (1H, m, CH), 4.10 (2H, m, OCH_2CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.14, 16.12, 20.80, 29.39, 42.82, 60.65, 69.13, 70.20, 80.71, 82.90, 173.53; IR: 3294, 2936, 1729, 1447, 1377, 1258, 1164, 1097, 1023, 735, 634. HRMS (FAB+): calcd. for $C_{11}H_{15}O_2$, 179.1072, found, 179.1072.



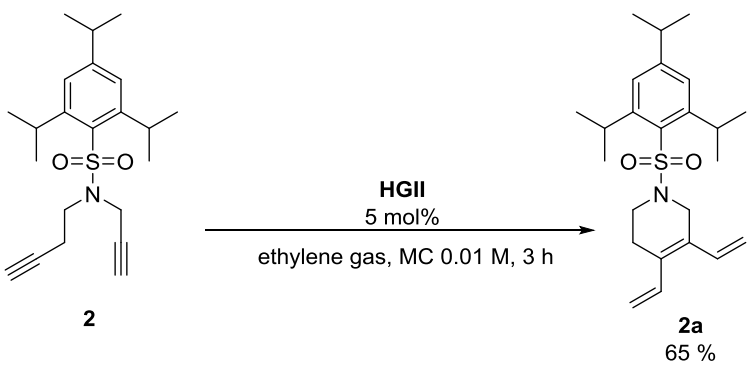
Scheme S4. Synthesis of Monomers **5** and **7**

5: Diethoxyhydrazine[15] (1 mmol, 176.2 mg) was added to the Ar-purged flask in DMF (6 ml). Cs_2CO_3 (2.2 mmol, 716.8 mg) and propargyl bromide in toluene solution (2.2 mmol, 0.16 ml) were added to the solution and the mixture was stirred for 12 h. The reaction mixture was quenched with NH_4Cl solution. Product was extracted with diehyl ether and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane = 1:10) to afford compound **5** as a colorless liquid (201.8 mg, 80 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.17 (6H, m, CH_2CH_3), 2.23 (2H, s, CC*H*), 4.10 (4H, m, OCH_2), 4.35 (4H, m, NCH_2); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.30, 39.35, 39.69, 40.66, 41.01, 62.58, 62.83, 72.83, 73.12, 77.48, 154.93; IR: 3289, 2985, 1714, 1413, 1379, 1275, 1229, 1095, 751, 678 cm^{-1}; HRMS (FAB+): calcd. for $C_{12}H_{17}N_2O_4$, 253.1188, found, 253.1186.

7: 4-*tert*-butylbenzohydrazide (1 mmol, 192.3 mg) was added to the Ar-

purged flask in THF (6 ml). Di-*tert*-butyl dicarbonate (1 mmol, 0.23 ml) was added to the solution. The reaction mixture was stirred for 1h at room temperature. Product was extracted with diethyl ether and the organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a white solid. Without further purification, it was dissolved in DMF (6 ml). Cs_2CO_3 (2.2 mmol, 716.8 mg) and propargyl bromide in toluene solution (2.2 mmol, 0.16 ml) were added to the solution and the mixture was stirred for 1 h. The reaction mixture was quenched with NH_4Cl solution. Product was extracted with diehyl ether and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane = 1:10) to afford compound **7** as a colorless liquid (320.6 mg, 87 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.30 (9H, s, ArC(C*H*$_3$)$_3$), 1.39 (9H, s, OC(C*H*$_3$)$_3$), 2.32 (2H, s, CC*H*), 4.34 (4H, br, NC*H*$_2$), 7.36 (2H, s, Ar), 7.50 (2H, s, Ar); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 26.96, 27.94, 28.93, 29.88, 31.24, 32.18, 34.80, 82.77, 124.28, 124.81, 126.60, 127.80, 131.05, 153.50, 172.14; IR: 3292, 2967, 1717, 1667, 1367, 1261, 1158, 848, 763, 663 cm^{-1}; HRMS (FAB+): calcd. for $C_{22}H_{29}N_2O_3$, 369.2178, found, 369. 2179.

General procedure for cyclopolymerization: Monomer (0.1 mmol) was weighed in a 4-ml sized screw-cap vial with septum and purged with argon. Anhydrous and degassed solvent (0.1 or 0.03 ml) was added to the vial. The solution of initiator (0.07 or 0.03 ml) was added at once under vigorous stirring. After confirming the monomer conversion by TLC, the reaction was quenched by excess amount of ethyl vinyl ether. The concentrated mixture was precipitated by methanol or hexane. The obtained red-orange colored solid was dried *in vacuo*.

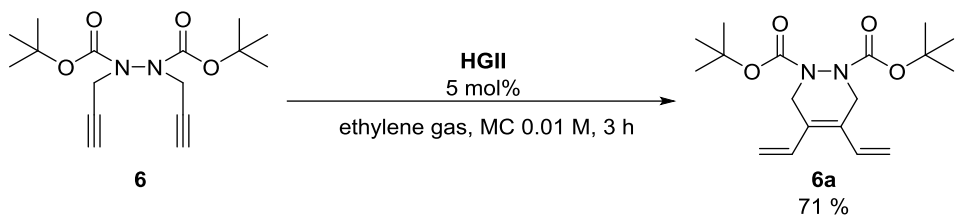


2 **2a** 65 %

Scheme S5. Intermolecular Enyne Metathesis of **2** and ethylene gas

2a: **2** (37.3 mg, 0.1 mmol) was added to the Ar-purged flask. Distilled and degassed DCM (9.5 ml) was added to the flask. 5 mol% of 2nd generation Hoveyda-Grubbs catalyst in DCM (0.5 ml) was added to the solution under vigorous stirring. After 1 h, the reaction was quenched by excess amount of ethyl vinyl ether. The concentrated crude reaction mixture was purified by

flash column chromatography on silica gel (EtOAc:Hexane = 1:30) to afford compound **2a** as white solid (26 mg, 65 %); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.23 (18H, m, CH(CH_3)$_2$), 2.41 (2H, t, J = 4 MHz, NCH$_2$CH_2), 2.89 (1H, m, CH(CH$_3$)$_2$), 3.35 (2H, t, J = 4 MHz, NCH_2CH$_2$), 3.89 (2H, s, NCH_2C), 4.19 (2H, m, CH(CH$_3$)$_2$), 5.15 (4H, m, CCHCH$_2$), 6.93 (2H, m, CCHCH_2), 7.15 (2H, s, Ar$_H$); ^{13}C-NMR (100 MHz): δ 23.53, 24.78, 25.56, 29.35, 34.41, 40.76, 43.31, 113.43, 114.61, 123.89, 128.37, 129.91, 131.00, 131.06, 132.25, 151.73, 153.25; IR: 2959, 2930, 2870, 1600, 1461, 1424, 1365, 1318, 1291, 1153, 1102, 1038, 942, 736, 677, 628 cm^{-1}; HRMS (FAB+): calcd. for $C_{24}H_{36}NO_2S$, 402.2467, found 402.2469.



Scheme S6. Intermolecular Enyne Metathesis of **6** and ethylene gas

6a: **6** (30.8 mg, 0.1 mmol) was added to the Ar-purged flask. Distilled and degassed DCM (9.5 ml) was added to the flask. 5 mol% of 2nd generation Hoveyda-Grubbs catalyst in DCM (0.5 ml) was added to the solution under vigorous stirring. After 3 h, the reaction was quenched by excess amount of ethyl vinyl ether. The concentrated crude reaction mixture was purified by

flash column chromatography on silica gel (EtOAc:Hexane = 1:20) to afford compound **6a** as white solid (23.9 mg, 71 %); ^{1}H-NMR (300 MHz, Benzene-d_6, 60 ℃): δ 1.44 (9H, s, $(CH_3)_3$), 3.87 (2H, d, J = 18 Hz, NCH_2), 4.80 (2H, br, NCH_2), 4.86 (4H, dd, J = 18, 12 Hz, $CHCH_2$), 6.58 (2H, dd, J = 18, 12 Hz, $CHCH_2$); ^{13}C-NMR (75 MHz, Benzene-d_6, 60 ℃): δ 28.06, 43.37, 80.48, 113.93, 129.60, 130.79, 153.93; IR: 2979, 1709, 1368, 1261, 1156, 750 cm^{-1}; HRMS (EI+): calcd. for $C_{23}H_{28}O_2$, 336.2049, found, 336.2053.

^{1}H-NMR characterization of polymers: Rotameric signals observed in ^{13}C-NMR spectrum of poly(**1**) and ^{1}H-NMR and ^{13}C-NMR spectra of poly(**6**) by amide bond coalesced at 60 ℃. Poly(**1**) was taken in CD_2Cl_2 because olefin signals of poly(**1**) was overlapped with benzene signal.

Poly(**1**): (400 MHz, CD_2Cl_2) 0.87 (6H, br s, $(CH_2)_4CH_3$ and CH_2CH_3), 1.26 (4H, br s, $CH_2(CH_2)_2CH_2$), 1.46 (2H, br s, $(CH_2)_3CH_2CH_3$), 1.62 (2H, br s, $CHCH_2CH_3$), 2.61 (3H, br m, CH_2CH_2C and $COCH$), 3.75 (2H, br m, NCH_2CH_2), 4.47 (2H, br m, NCH_2C), 7.02 (2H, br m, H_{olefin}).

Poly(**2**) (500 MHz, $CDCl_3$): 1.24 (18H, br s, $CH(CH_3)_2$), 2.53 (2H, br m, CH_2CH_2C), 2.89 (1H, br s, $CH(CH_3)_2$), 3.30 (2H, br m, NCH_2CH_2), 4.15 (4H, br m, NCH_2C and $CH(CH_3)_2$), 6.84 (2H, br m, H_{olefin}), 7.16 (2H, br s,

Ar_H).

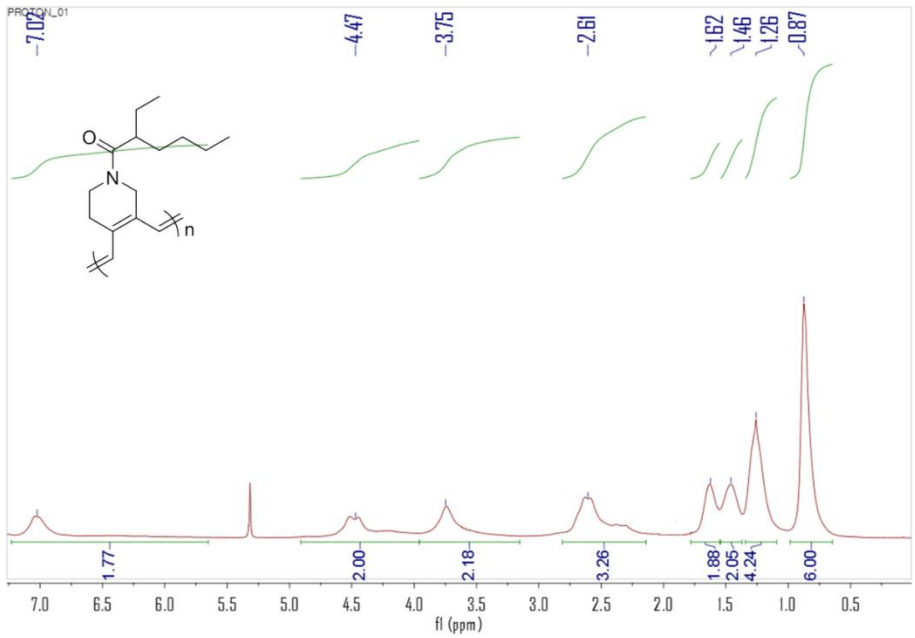
Poly(**3**) (500 MHz, $CDCl_3$): 1.22 (6H, br m, CH_2CH_3), 2.67 (6H, br m, CH_2CH_3 and CH_2CH_2C), 3.26 (2H, br m, NCH_2CH_2), 3.92 (2H, br m, NCH_2C), 7.10 (5H, br m, H_{olefin} and Ar_H).

Poly(**5**) (500 MHz, benzene-d_6, 60 ℃): 1.12 (6H, br m, CH_2CH_3), 4.16 (6H, br m, CH_2CH_3 and NCH_2), 5.05 (2H, br m, NCH_2), 6.78 (2H, br m, H_{olefin}).

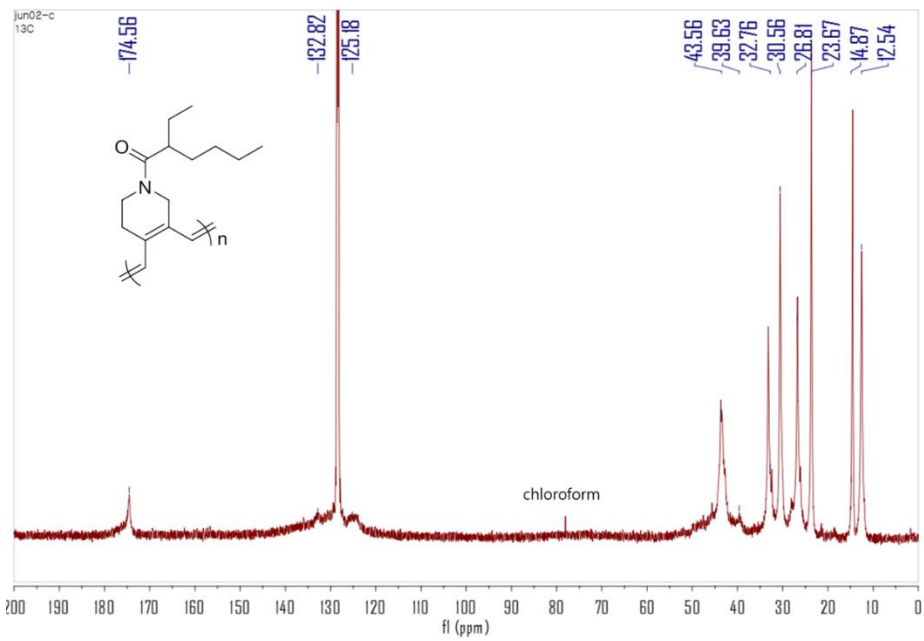
Poly(**6**) (300 MHz, benzene-d_6, 60 ℃): 1.66 (18H, br m, $C(CH_3)_3$), 4.15 (2H, br m, NCH_2), 5.06 (2H, br m, NCH_2), 6.82 (2H, br m, H_{olefin}).

Poly(**7**) (500 MHz, benzene-d_6, 60 ℃): 1.19 (18H, br m, p-$(CH_3)_3Ar$ and $C(CH_3)_3$), 4.24 (2H, br m, NCH_2), 5.20 (2H, br m, NCH_2), 6.89 (2H, br m, H_{olefin}), 7.33 (2H, br m, Ar_H), 7.82 (2H, br m, Ar_H).

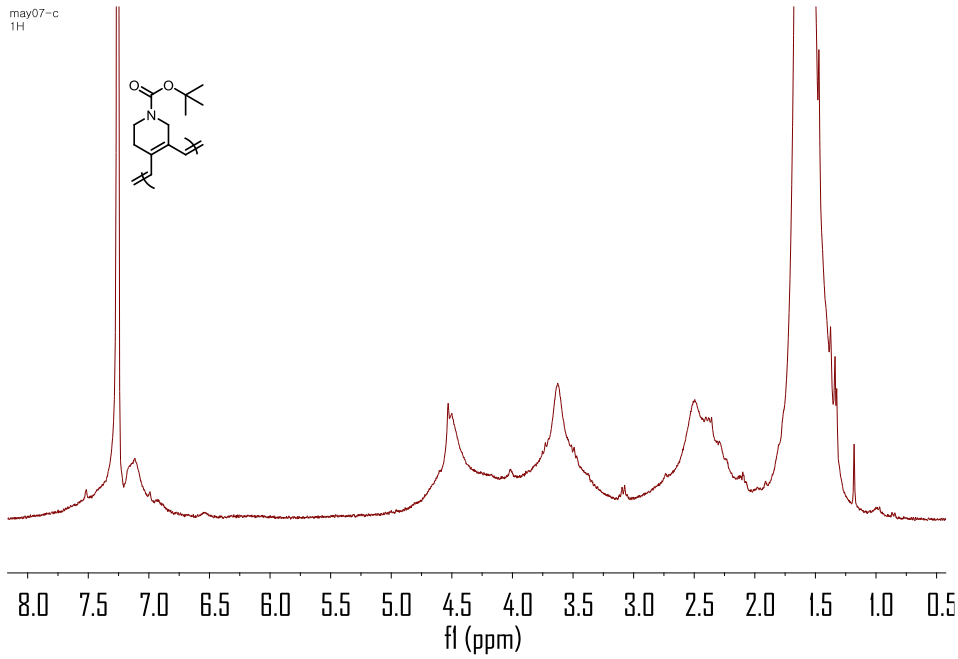
Figure S1. ^{1}H−NMR and ^{13}C−NMR spectra of homopolymers Poly(**1**) in CD_2Cl_2



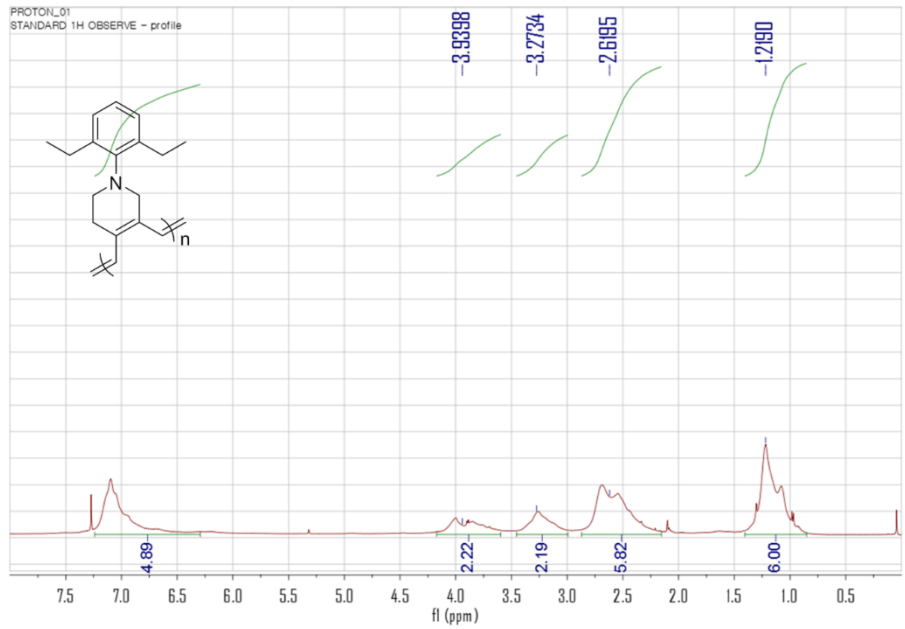
In benzene−d_6 at 60 ℃

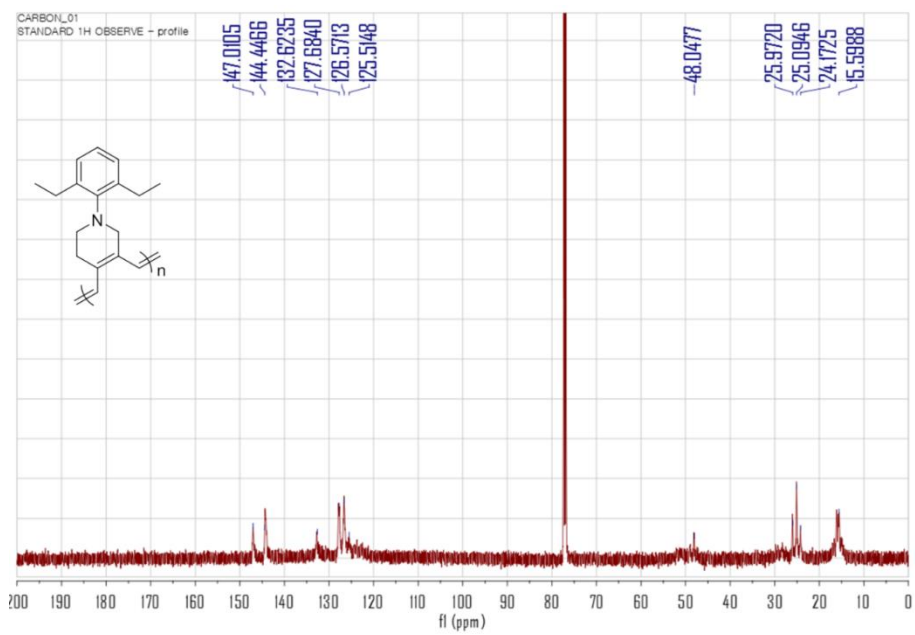


Poly(**3**) in benzene-d_6 at 60℃

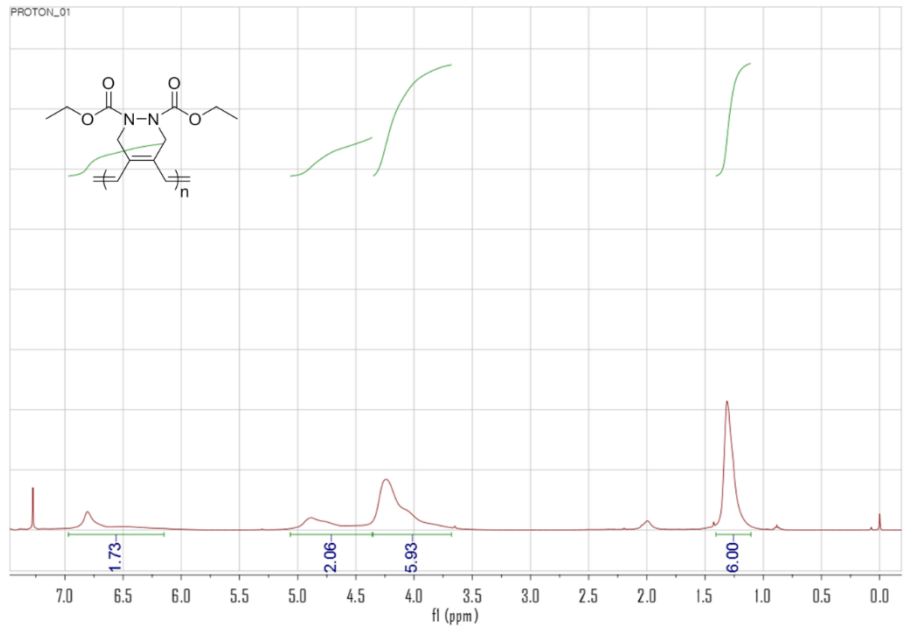


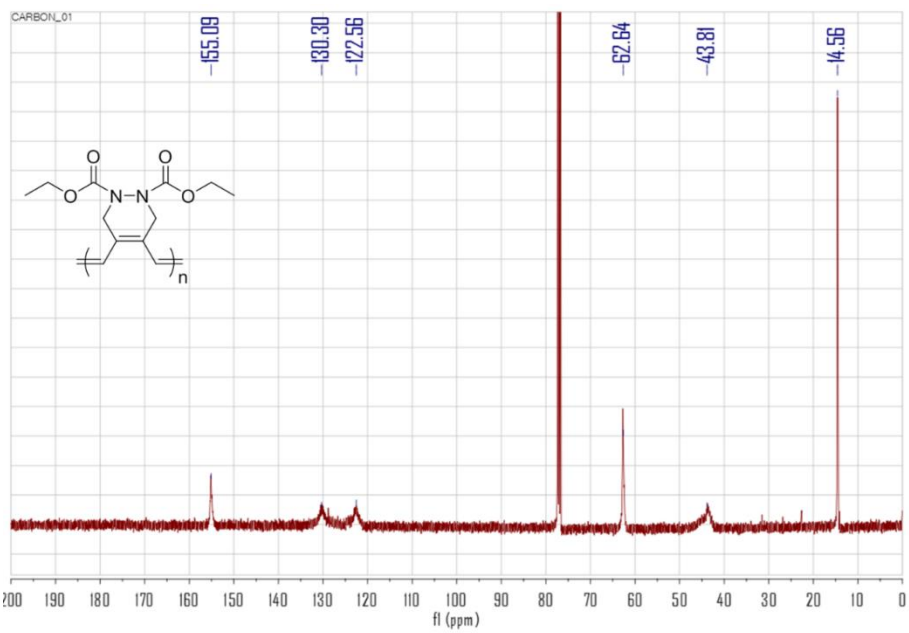
Poly(**4**) in $CDCl_3$



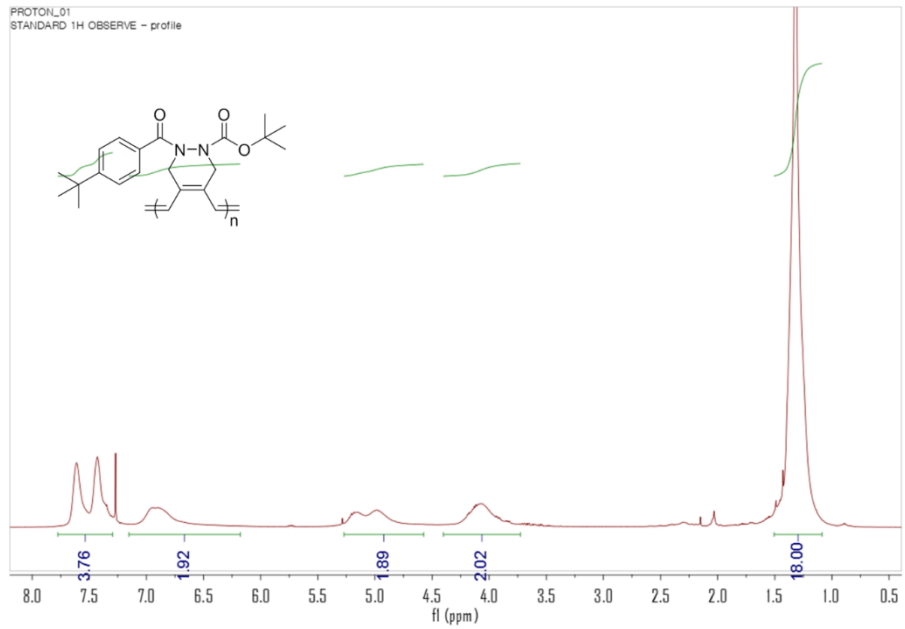


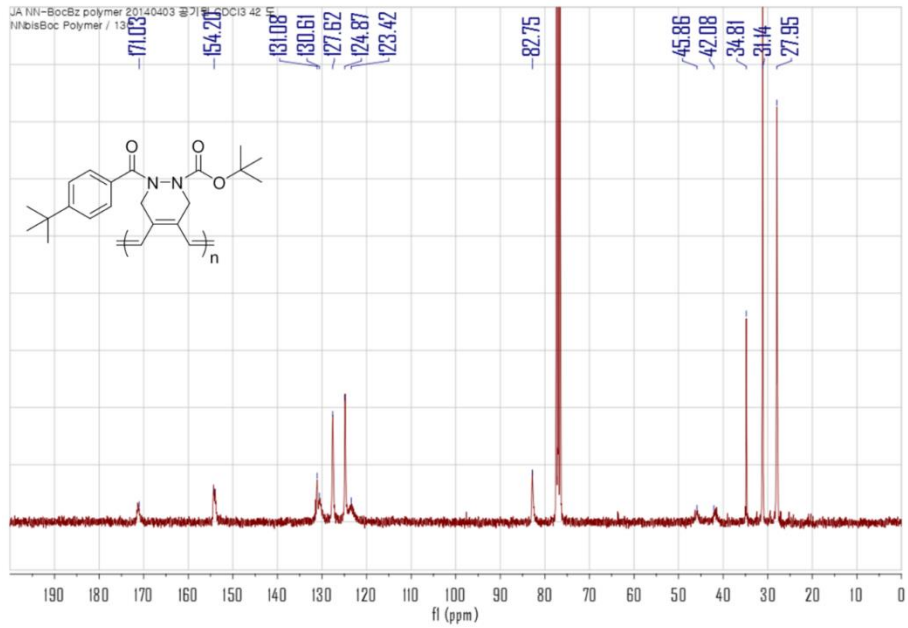
Poly(**5**)


PROTON_01
1.73
2.06
5.93
6.00
f1 (ppm)

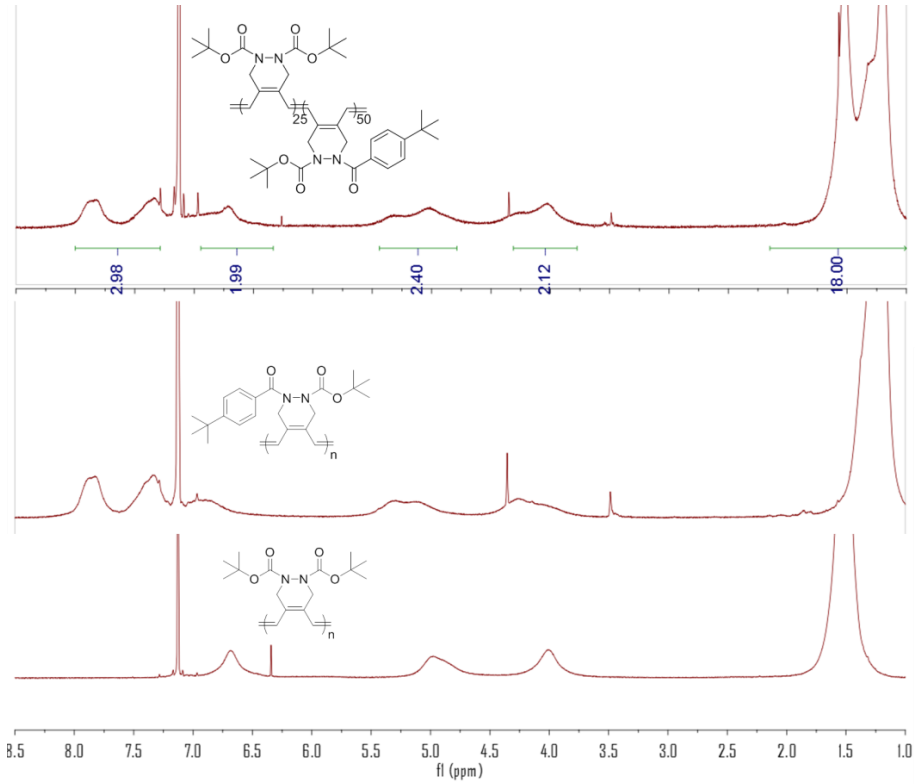

CARBON_01
155.09
130.30
122.56
62.64
43.81
14.56
f1 (ppm)

Poly(**7**)

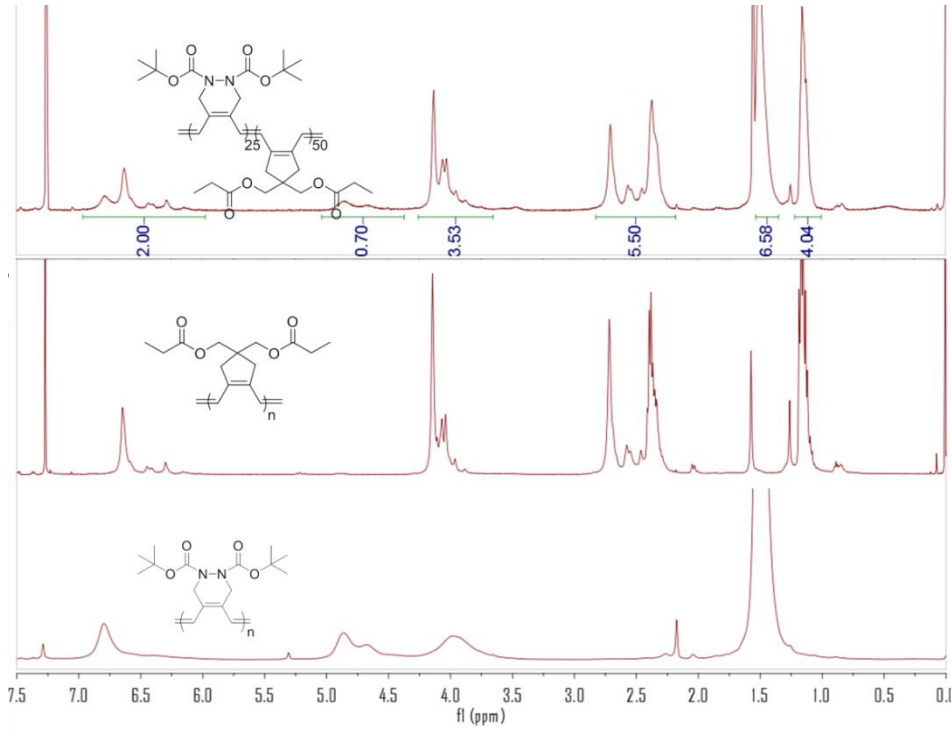

PROTON_01
STANDARD 1H OBSERVE – profile
3.76
1.92
1.89
2.02
18.00
f1 (ppm)


171.03
154.20
131.08
130.61
127.62
124.87
123.42
82.75
45.86
42.08
34.81
31.14
27.95
f1 (ppm)

Poly(**6**)–*b*–poly(**7**) in benzene–d6 at 60 ℃



Poly(**6**)–*b*–poly(**8**) in $CDCl_3$



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Chapter 3. Cyclopolymerization of 1,8-nonadiyne derivatives

3.1 Abstract

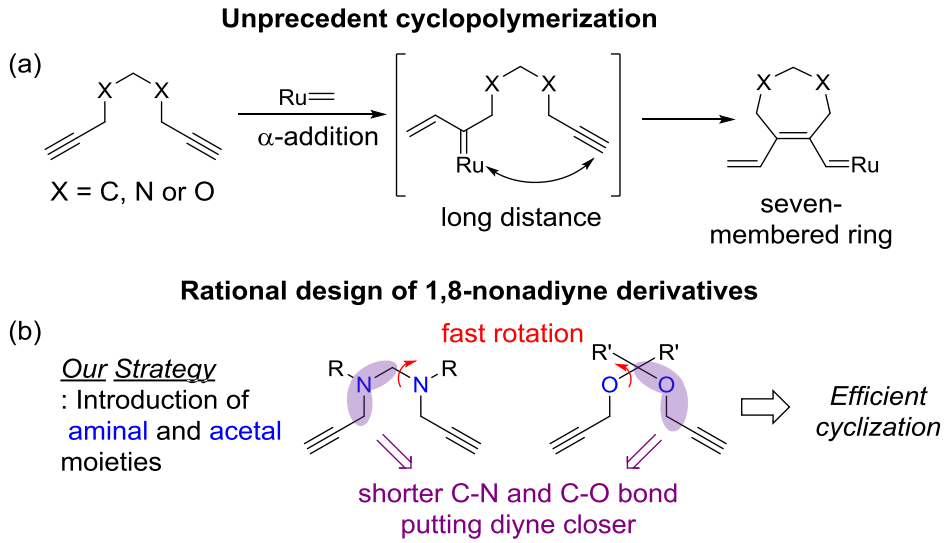
Studies into the cyclopolymerization (CP) of diyne derivatives using metal carbenes have focused on the formation of five- and six-membered rings because these small rings can be easily synthesized while the preparation of medium-sized seven-membered rings are more difficult. For the first time, we achieved the CP forming challenging seven-membered rings as repeat units using Grubbs catalysts by novel design of 1,8-nonadiyne monomers. The key to the successful CP was the introduction of the appropriate aminal and acetal groups, which have short C-N and C-O bonds, and low rotational barriers, thus greatly enhancing the cyclization efficiency. During our mechanistic investigation, we directly observed an actual 14-electron Ru propagating carbene by ^{1}H NMR spectroscopy for the first time during olefin metathesis reaction, presumably because the great steric hindrance from the propagating carbene containing a larger seven-membered ring than five- or six-membered ring retarded the coordination of ligands. We also observed decomposition of the catalysts to ruthenium hydrides during polymerization for the first time. Kinetic studies revealed three interesting features of this 1,8-nonadiyne CP: i) in contrast to conventional polymerizations, the rate-determining step for the CP of 1,8-nonadiynes was the cyclization step; ii)

the intrinsic reactivity of the acetal monomers was higher than that of the aminal monomers; but iii) the overall polymerization efficiency of the aminal monomers was higher than that of the acetal monomers because of the higher stability of their carbenes. Finally, we achieved a controlled CP of the aminal monomers using a fast-initiating third-generation Grubbs catalyst. This allowed the synthesis of not only the diblock copolymer containing five- and seven-membered rings, but also the triblock copolymer containing five-, six-, and seven-membered rings.

3.2 Introduction

Although medium-sized rings, such as seven-membered rings, are common and important moieties in many natural products and novel pharmaceuticals, their construction is more challenging than that of small rings. Among the various methods developed to prepare seven-membered rings,[1] olefin metathesis reactions, such as ring-closing metathesis (RCM) and ring-closing enyne metathesis (RCEYM), have been employed as the key step.[2] There is one report on Rh-catalyzed diyne cyclopolymerization, which gives a wide-bandgap polyene containing seven-membered rings via an insertion mechanism but it yielded low molecular weight polymers with a maximum number-average molecular weight (M_n) of 6.5 kDa due to its poor efficiency.[3] This led us to wonder if 1,8-nonadiynes could be cyclopolymerized using Grubbs catalysts to prepare conjugated polyenes containing seven-membered rings via selective α-addition (Scheme 3.1a). Although the CP of 1,8-nonadiynes is expected to be even more challenging[4] than that of 1,7-octadiynes, rational and novel design of the monomers would lead to their successful CP. In this section, we report the first successful CP of 1,8-nonadiynes to give seven-membered rings using Grubbs catalysts, through the introduction of aminal and acetal groups to facilitate cyclization of the

medium rings (Scheme 3.1b). Controlled CP of the aminal monomers was also possible, thus allowing the synthesis of a triblock copolymer containing five-, six-, and seven-membered rings in series. Furthermore, extensive kinetic experiments revealed many distinct unprecedented mechanistic features of CP.

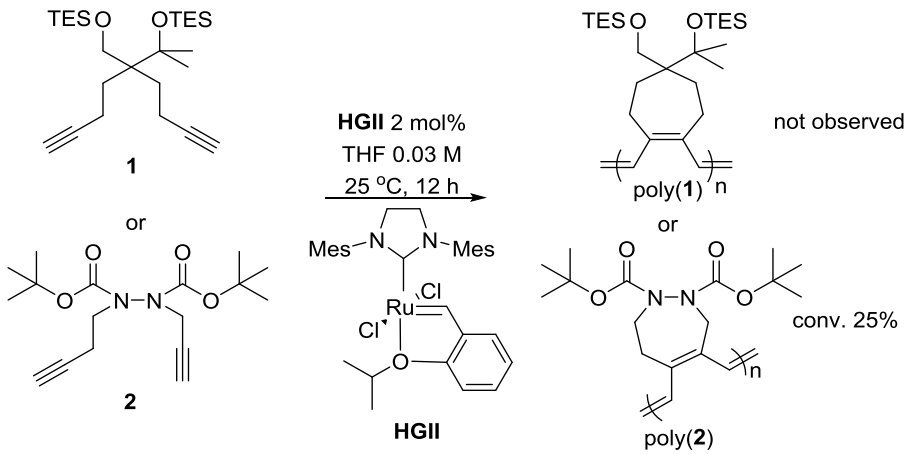


Scheme 3.1 (a) Cyclopolymerization of 1,8-nonadiyne and (b) a schematic representation of our key strategy.

3.3 Results and Discussion

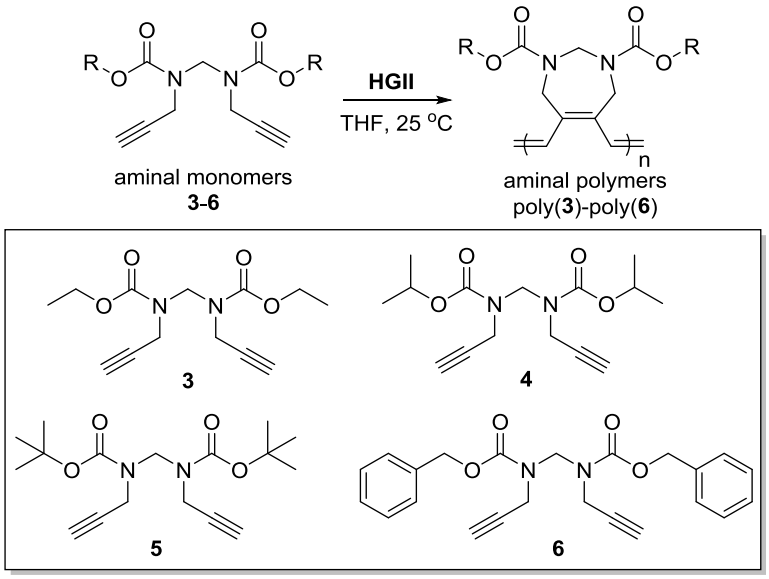
3.3.1 Cyclopolymerization of Various 1,8-Nonadiynes

As our initial attempt, we prepared 1,8-nonadiyne derivatives **1** and **2** bearing the same sterically bulky side chains as our previous 1,7-octadiyne monomers[5] and hoped that this enhanced Thorpe-Ingold effect would facilitate the medium-ring formation (Scheme 3.2). However, the treatment of the monomer **1** with 2 mol% of the second-generation Hoveyda-Grubbs catalyst (**HGII**)[6] in tetrahydrofuran (THF) did not yield the desired polymer, while CP of a hydrazide monomer **2** containing the shorter C-N bond (1.47 Å) led to a somewhat improved conversion of 25%. However, CP of monomer **2** remained limited, as the CO-N-N-CO dihedral angles of *N*-substituted diacylhydrazines are ~90° in their most stable conformations, and the rotational barrier is relatively high (E_a = ~19 kcal/mol).[7] We therefore concluded that unfavorable rotation of the N-N bond in the hydrazide monomer **2** led to a less efficient cyclopolymerization.[8]



Scheme 2. Unsuccessful cyclopolymerization of monomers 1 and 2

Table 3.1 Cyclopolymerization of aminal monomers 3–6



Entry	Monomer	[M]/[I]	Conc. (M)	Time (h)	Mn (kDa)[a]	PDI[a]	Conv. (%)[b]	Yield (%)[c]
1	3	50	0.03	16	15.2	1.49	97	85
2	3	100	0.03	24	24.0	1.57	73	58
3	4	50	0.06	16	17.7	1.61	99	72
4	4	100	0.1	24	20.6	1.82	69	49
5[d]	5	50	0.2	16	16.0	1.49	91	78
6[d]	5	100	0.2	24	28.1	1.86	70	62
7	6	50	0.1	12	17.4	2.18	99	95

[a] Determined by chloroform SEC calibrated using polystyrene (PS) standards. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yield after purification. [d] 3,5-Dichloropyridine (20 mol% to the monomer) was added.

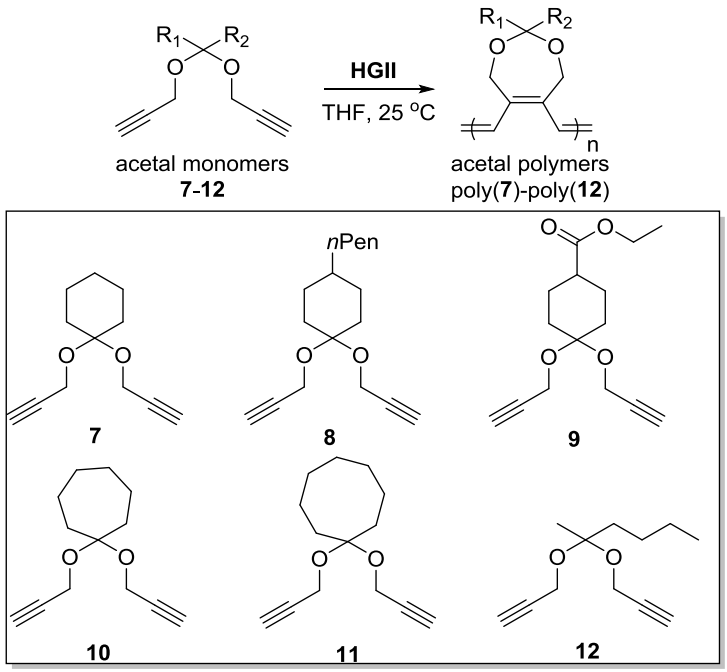
To improve the CP efficiency, we designed new monomers **3**–**6** (Table 3.1) through the introduction of an aminal group, which contains N–C–N bonds with shorter C–N bonds, in addition to a low rotational barrier. Initially, the CP of ethyl carbamate–containing monomer **3** was attempted in the presence of 2 mol% **HGII** at various concentrations of THF. The reaction in 0.6 M afforded 30% conversion after 3 h, while lowering the concentration to 0.03 M afforded a higher conversion to the desired polymer (67%, Table S1). Increasing the reaction time to 16 h further increased the conversion to 97%, and the polymer with a high M_n of 15.2 kDa was isolated in 85% yield (Table 3.1, entry 1). When the monomer feed ratio increased to 100 (i.e., 1 mol% **HGII**), CP still proceeded well to give poly(**3**) with a high M_n of 24.0 kDa in 73% conversion (Table 3.1, entry 2). Monomer **4**, bearing the larger *iso*–propyl side–chain, was also successfully cyclopolymerized in conversions of 99% and 69% at M/I = 50 and 100, respectively (with M_n of 17.7 and 20.6 kDa, respectively) (Table 3.1, entries 3 and 4). In addition, in the case of monomer **5** containing the larger *tert*–butyl side–chain, the addition of a small amount of 3,5–dichloropyridine (20 mol%) to improve the CP yielded the corresponding poly(**5**) with high M_n of 16.0 and 28.1 kDa at M/I = 50 and 100, respectively (91% and 70% conversion) (Table 3.1, entries 5 and 6).

Finally, benzyl- containing poly(**6**) was prepared in 99% conversion with an M_n of 17.4 kDa at M/I = 50/1 (Table 3.1, entry 7). In short, although a relatively long reaction time was required, the CP of various aminal-containing 1,8-nonadiynes successfully produced the unprecedented medium-ring-containing polyenes using a Grubbs catalyst.

To accelerate the CP of the 1,8-nonadiynes, we designed a new series of monomers (**7 – 12**, Table 3.2) via the introduction of acetal groups in which the C-O bond was even shorter (1.43 Å) than the C-N bond and the rotational barrier of the O-C-O bonds was also very low (Table 3.2, entries 1 – 7). Initially, the CP of the cyclohexyl acetal-containing monomer **7** provided an insoluble polymer due to low solubility (Table 3.2, entry 1). To prepare soluble polymers, monomer **8**, containing an additional *n*-pentyl group on the cyclohexyl ring, was polymerized by **HGII** at M/I = 30 and after 4 h, the soluble poly(**8**) with an M_n of 8.2 kDa was isolated in 97% yield (99% conversion, entry 2). Analogous poly(**9**) containing ester group was also obtained with 79% conversion in 5 h (M/I = 30, entry 3). In addition, the CP of the cycloheptyl- and cyclooctyl-containing monomers **10** and **11** bearing wider bond angles than 109.5° of cyclohexyl group gave 88% and 93% conversions in 6 h and 4 h, respectively (M/I = 40, entries 4 and 5).

Furthermore, the acyclic alkyl acetal-containing monomer **12** was also polymerized with 80% conversion to give poly(**12**) in 4 h (M/I = 40, entry 7). With the most reactive monomer **11**, we increased the monomer feed ratio up to 50, but the conversion was 65% (entry 6), indicating that it was more difficult to produce polyenes with high molecular weights by the CP of acetal monomers compared to that of the aminal monomers.

Table 3.2 Cyclopolymerization of aminal monomers **7**–**12**



Entry	Monomer	[M]/[I]	Conc. (M)	Time (h)	Mn (kDa)[a]	PDI[a]	Conv. (%)[b]	Yield (%)[c]
1	**7**	30	0.03	4	Insoluble polymer			
2	**8**	30	0.03	4	8.2	2.33	99	97
3	**9**	30	0.03	5	5.3	1.99	79	64
4	**10**	40	0.06	6	6.6	4.49	88	87
5	**11**	40	0.06	4	5.9	3.12	93	66
6	**11**	50	0.06	8	6.0	4.29	65	62
7	**12**	30	0.06	4	4.4	1.69	80	47

[a] Determined by chloroform SEC calibrated using polystyrene (PS) standards. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yield after purification.

Although the CP of 1,8-nonadiynes using a Grubbs catalyst should undergo α-addition to form seven-membered rings, the possibility of eight-membered ring formation via β-addition cannot be completely ruled out. We therefore confirmed the microstructures of the prepared conjugated polyenes by analysis of ^{13}C NMR spectrum in chlorobenzene-d_5, because the signals by rotamers from the carbamate groups coalesced into single peak at 90 ° C (see Figure 3.1a and Figure 3.2). As shown in the figures, signals corresponding to the allylic carbon (A) adjacent to the nitrogen and signals corresponding to the carbon (B) between the two nitrogens appeared at 45.85 and 60.90 ppm, respectively, and the signal corresponding to the carbonyl carbon (C) appeared as a single peak at 155.25 ppm, thus confirming that poly(**3**) contained a single ring size. In addition, we independently synthesized an analogous model compound bearing a seven-membered ring (**3′**) via RCM to compare its ^{13}C NMR spectrum with that of poly(**3**) (for the RCM reaction, see Scheme S5). As shown in Figures 3.1a and 1b, poly(**3**) and the model compound **3′** shared common chemical shifts in their ^{13}C NMR spectra (i.e., 155.3 vs. 155.6 ppm, 61.7 vs. 61.4 ppm, 45.9 vs. 44.4 ppm, and 14.6 vs. 14.6 ppm). All other aminal-containing polymers showed similar patterns (Figure S8), indicating that these polyenes have seven-membered rings as the

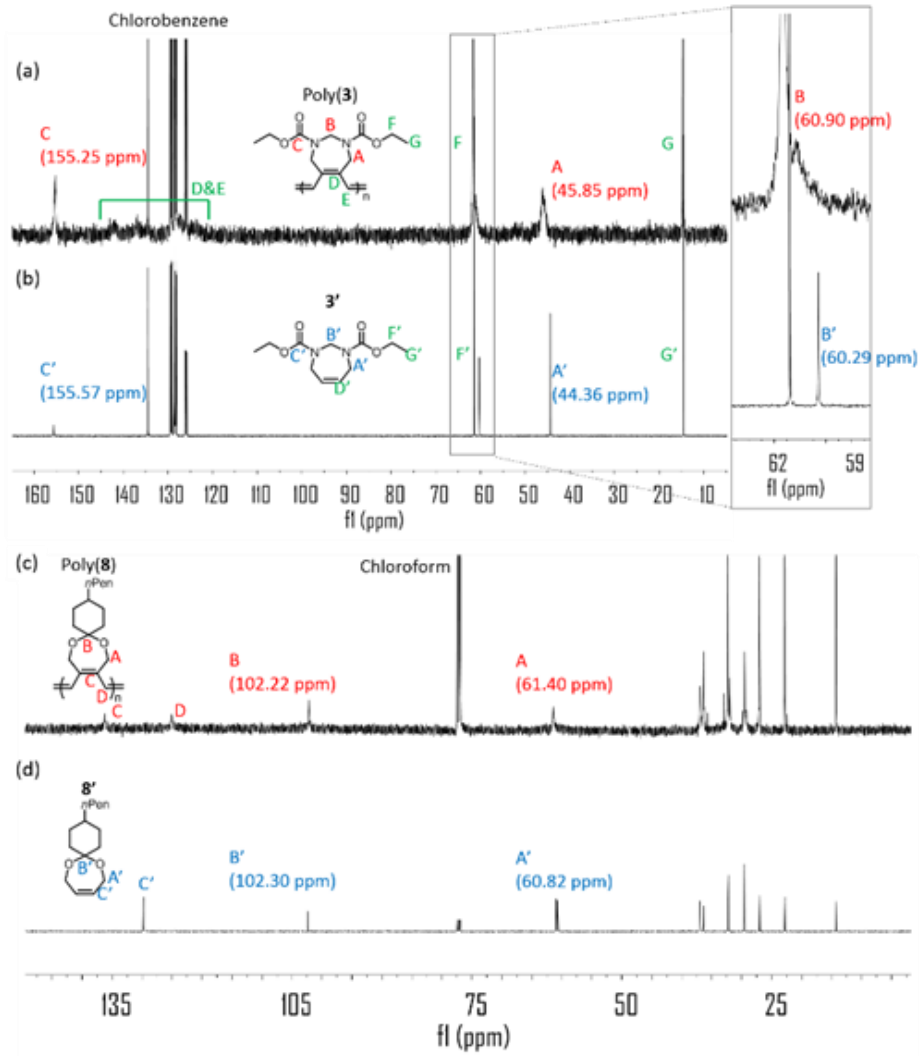


Figure 3.1 ^{13}C NMR Spectra of (a) poly(**3**) and (b) **3′** in C_6D_5Cl at 90 ° C, and (c) poly(**8**) and (d) **8′** in $CDCl_3$ (see Figure S8).

repeat unit constructed via exclusive α −addition. The microstructure of the acetal-containing polyenes was also confirmed by similar means. Signals corresponding to the allylic carbon (A and A′) and the quaternary carbons (B

and B′) exhibited similar chemical shifts (i.e., 102.2 vs. 102.3 ppm and 61.4 vs. 60.8 ppm) from ^{13}C NMR spectra of poly(**8**) and **8′** (Figures 1c and 1d), again confirming the seven-membered ring as the repeat unit. To thoroughly confirm the regioselectivity, we designed the 1:1 reaction of aminal-containing mono-alkyne **13** and **GIII** in 0.02 M THF-d_8 and monitored a carbene by ^1H NMR spectroscopy (Figure 3.2).[9] In this reaction, a new propagating carbene will be observed only when β -addition occurs (**13**β,

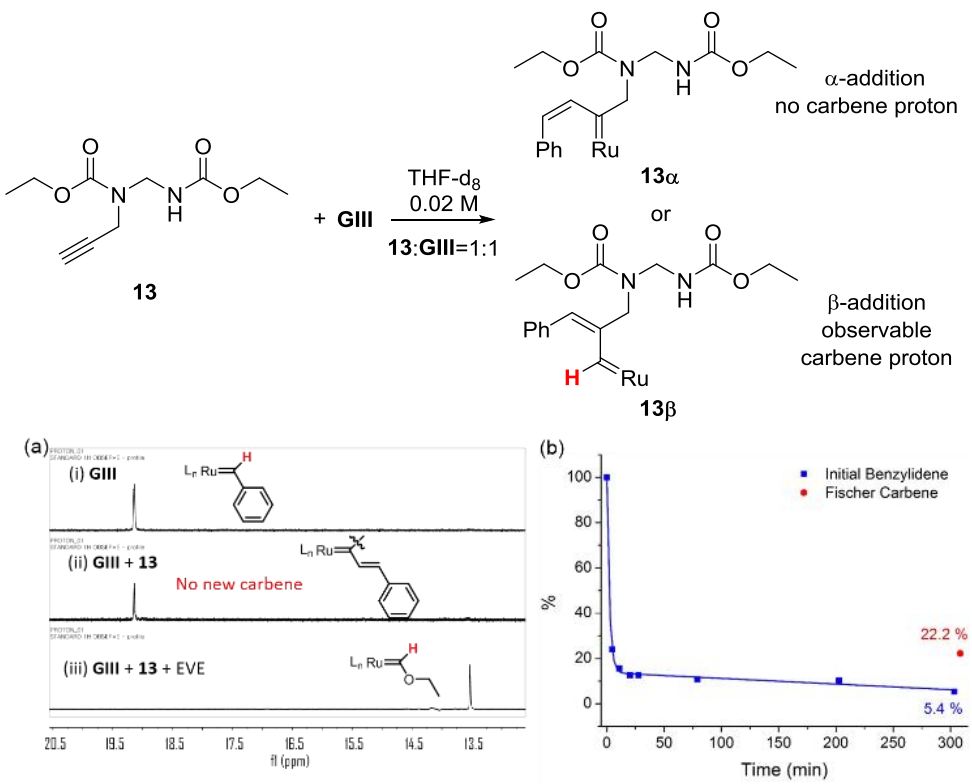


Figure 3.2 Monitoring of 1:1 Reaction of **13** and **GIII**: (a) ^1H NMR spectra of carbene and (b) plot of carbene% over time.

Figure 3.2). As expected, no new propagating carbene was detected during the reaction and the the initial benzylidene was consumed (Figure 3.2a). After terminating the reaction with ethyl vinyl ether (EVE),[10,11] the remaining initial benzylidene peak disappeared and the Fischer carbene peak appeared at 13.5 ppm with four-time larger amount (22.2%) than the remaining initial benzylidene (5.4%) (Figure 2a and 2b). This increase would stem from the invisible propagating carbene via α-addition (**13α**, Figure 3.2). From these results, we concluded that CP of 1,8-nonadiyne derivatives produced seven-membered rings as repeat units via exclusively α-addition.

To explore the origin of the reactivity difference between the aminal and acetal monomers, we monitored the initial rates of CP of monomers **3**, **7**, and **11** using 10 mol% **HGII** in 0.1 M THF-d_8 by ^{1}H NMR spectroscopy. To our surprise, all monomers were consumed linearly over time, showing zeroth order kinetics, unlike previously reported examples that exhibited conventional 1st order kinetics (Figure 3.3a).[9,12] This result, in combination with our observation that a lower concentration gave higher conversion, implied that the rate-determining step (RDS) for the CP of 1,8-nonadiynes was cyclization, not intermolecular propagation.[13] In other words, RDS of CP

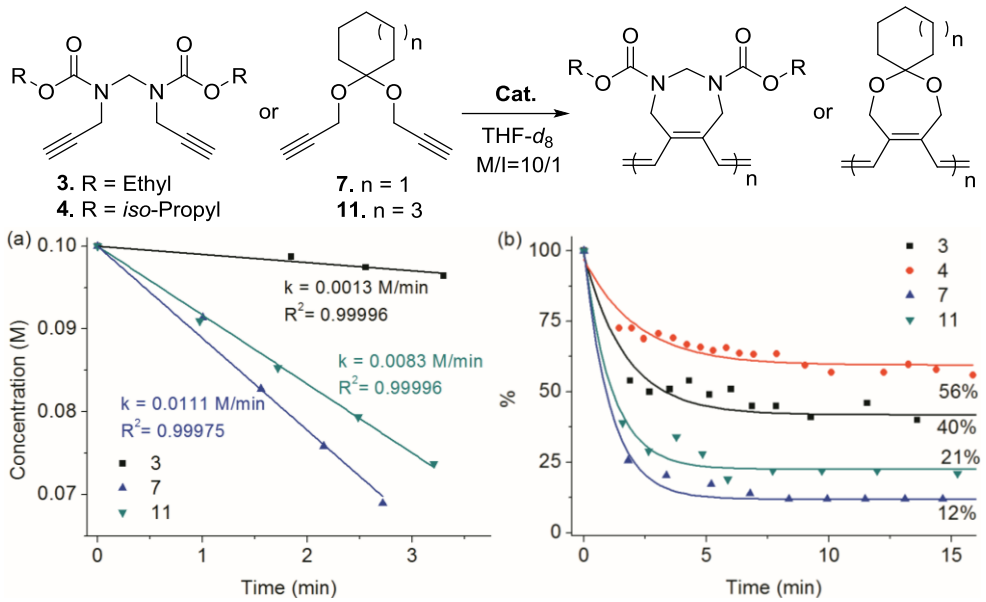


Figure 3. Kinetic analysis of (a) monomer consumption, and (b) decay of the propagating carbene over time.

forming five- or six-membered rings was the propagation step because of their fast cyclization while RDS of CP forming seven-membered rings was the intramolecular cyclization because of much slower cyclization. As expected from the data shown in Tables 1 and 2, the rate constants (k) for the propagation of acetal monomers **7** and **11** (0.0083 M/min and 0.0111 M/min) were up to 8.5 times higher than that of the aminal **3** (0.0013 M/min), because cyclization of the acetal monomers containing the shorter C-O bond was faster than that of the aminal monomers. We then questioned why the overall polymerization efficiency for CP of the acetal monomers was ironically lower,

despite their fast propagation rates. To explain this, we monitored the lifetimes of their propagating carbenes during their CP with the fast-initiating catalyst **GIII** (M/I = 10) in 0.2 M THF-d_8 using ^{1}H NMR spectroscopy (Figure 3b). The propagating carbenes from the four different 1,8-nonadiyne monomers (i.e., **3**, **4**, **7**, and **11**) were observed at 15.0-15.5 ppm. Decay of the propagating carbene generated from acetal monomers **7** and **11** was faster than that from aminal monomers **3** and **4**: after 15 min, the percentages of surviving propagating carbene (carbene%) during the CPs of aminals **3** and **4** were 40% and 56%, respectively, while those detected during the CPs of acetals **7** and **11** were significantly lower (i.e., 12% and 21%, respectively) (Figure 3b), thus implying their shorter lifetime. These data therefore account for the lower turnover numbers of the acetal monomers producing polyenes with lower molecular weight, despite their faster polymerization.

3.2.2 Mechanistic Investigations

In general, the proton signals for 16-electron or 18-electron Ru-based conjugated carbenes appear between 19 and 20 ppm in their ^{1}H NMR spectra,[9,14] but, during the CP of 1,8-nonadiynes by **GIII**, the corresponding signals for the new propagating carbenes appeared in the unusual range of

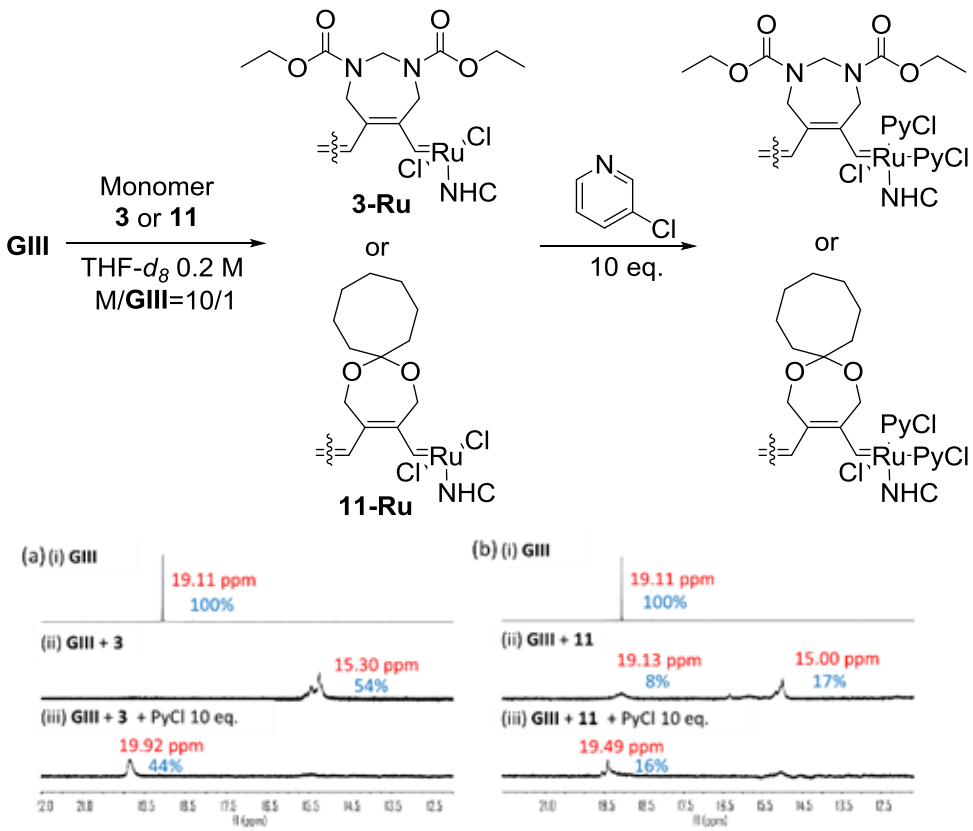
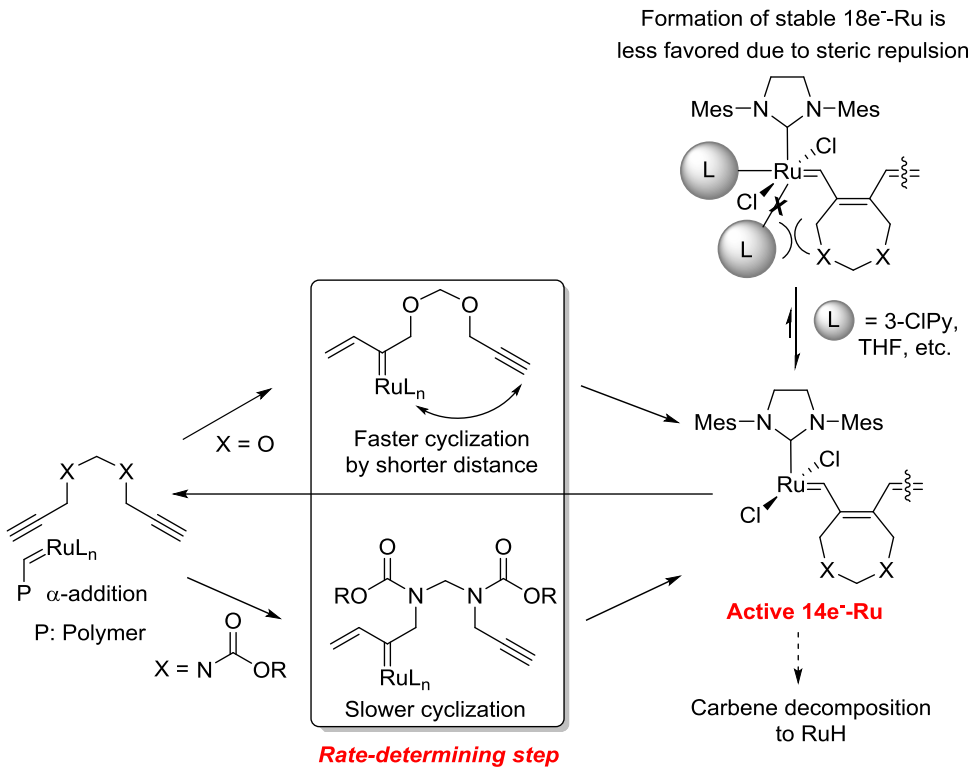


Figure 3.4 ^{1}H NMR spectra of the propagating carbenes during the reactions with (a) aminal **3** and **GIII**, (b) acetal **11** and **GIII**.

15.0 – 15.5 ppm (Figures 3.4a and 3.4b). As a control experiment, we monitored the same CP of monomers **3** and **11** using **HGII**, which has no additional L-type ligands, and observed comparable chemical shifts of 15.3 and 15.0 ppm, respectively, for the propagating carbene (Figure S1). This result suggests that the propagating carbene at 15.0 – 15.5 ppm was a 14-electron Ru ($14e^-$ – Ru) complex, the actual active propagating carbene

containing no stabilizing L-type ligands. Indeed, these $14e^-$-Ru active intermediates of carbenes have been difficult to observe due to their short lifetimes but the $14e^-$-Ru complex containing two *tert*-butoxides as X-type ligands was prepared by the Grubbs group, and the signal corresponding to its carbene proton was observed at 15.5 ppm[15], just like our observation. Formation of these $14e^-$-Ru complexes was further confirmed by the addition of an excess amount of the L-type ligand to make them well-studied 18-electron Ru complexes (Figures 3.4a and 3.4b). When we added 10 eq. 3-chloropyridine (PyCl) to the original reaction of aminal **3** and 10 mol% **GIII** in THF-d_8, the original signal at 15.30 ppm corresponding to the $14e^-$-Ru complex (carbene% of 54%) shifted to 19.92 ppm (i.e., the expected chemical shift for an 18-electron Ru complex) with a carbene% of 44% as monitored by ^{1}H NMR (Figure 3.4a). Interestingly, during the reaction with acetal **11** and 10 mol% **GIII**, two propagating species appeared at 15.00 ppm (a major, 17%) and 19.13 ppm (a minor, 8%), and both shifted to a new combined peak at 19.49 ppm upon the addition of 10 eq. PyCl (Figure 3.4b). We reasoned that the minor broad peak at 19.13 ppm originated from the dynamic equilibrium between the 14- and 18-electron Ru carbene complexes (Figure 3.4b and Scheme 3).

Scheme 3.3 Plausible reaction pathways



To verify this dynamic equilibrium, we selected another aminal monomer **7** and repeated the reaction with 10 mol% **GIII** in THF-d_8 to produce a propagating carbene with a similar broad peak at 19.27 ppm, which did not overlap with the initial benzylidene peak at 19.11 ppm. We monitored changes in the chemical shift of the two propagating carbenes generated upon the addition of increasing amounts of PyCl (1 – 10 eq.) by ^{1}H NMR spectroscopy (Figure 5). The minor peak at 19.27 ppm gradually increased in intensity and

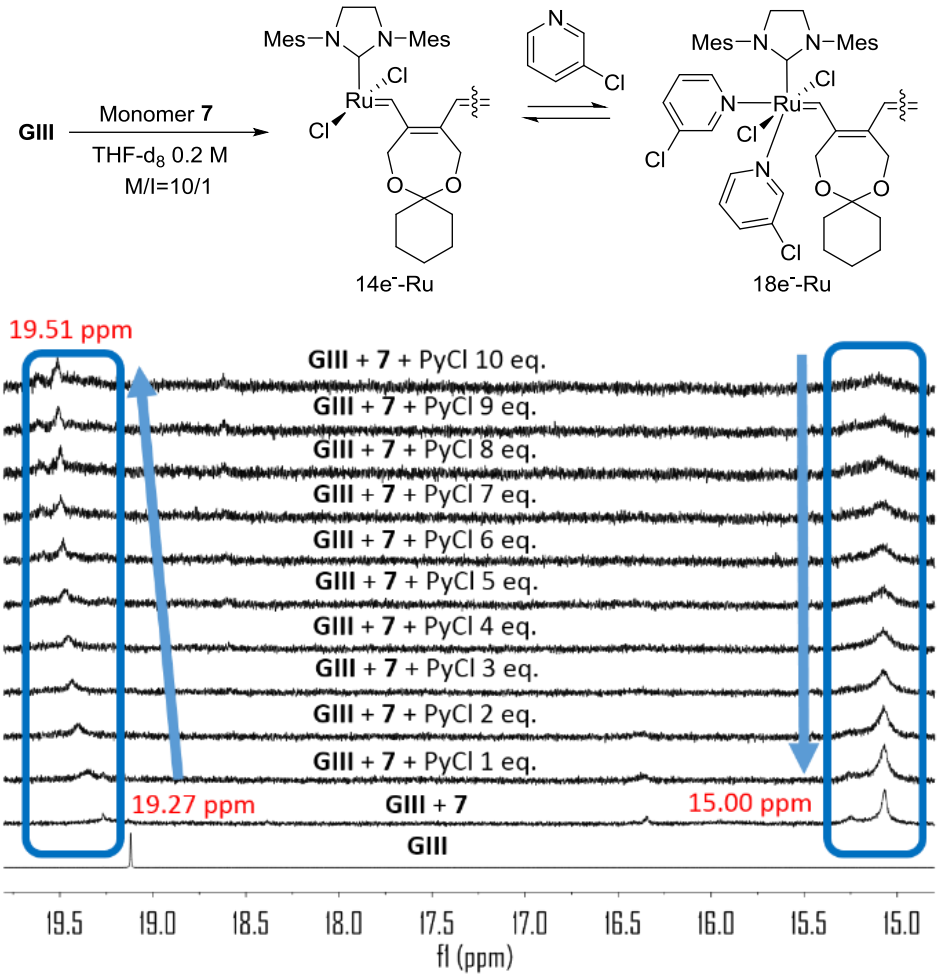


Figure 3.5 Changes in the ^{1}H NMR spectra during the reaction of **GIII** and monomer **7** upon the addition of gradually increasing amounts of PyCl.

shifted to 19.51 ppm, accompanied by a concomitant decrease in the intensity of the major peak at 15.00 ppm, due to the active coordination of increasing amounts of PyCl to the 14e^{-} – Ru complex shifting the equilibrium towards the 18 – electron Ru species. These observations further confirmed that the

propagating carbene appearing in the range of 15.0 – 15.5 ppm was indeed the active 14e⁻ – Ru propagating carbene bearing no extra ligands. As outlined in Scheme 3, the larger effective size of the seven- membered ring with wider angle than five- or six-membered ring adjacent to the Ru carbene would prevent the coordination of ligands such as pyridine, which contrasts to the case during the CP of 1,6-heptadiynes and 1,7-octadiynes. Furthermore, minor peaks (at 19.13 and 19.27 ppm for **11** and **7**, respectively) were only observed during the CP of the acetal monomers because the relatively smaller ether group in the acetals (Figure 3.4, **11-Ru**) than the carbamate group in the aminals (Figure 3.4, **3-Ru**) allowed the partial coordination of PyCl to the 14e⁻ – Ru complex.

However, this active 14e⁻-Ru species without any stabilizing ligands would readily decompose because of their lower stability than 18 – electron Ru species. For the last decade, we had no idea on to what they decomposed[16] but now for the first time, we observed the decomposed Ru complex assigned as a ruthenium hydride (RuH)[17] complex at −7.7 ppm during the CP of monomers **3** and **11** using **HGII** in THF-d_8 (M/I = 20) (Figures 3.6a and 6c). While monitoring the polymerization of aminal **3**, the signals corresponding to the propagating carbene at 15.3 ppm and to RuH at −7.7 ppm gradually

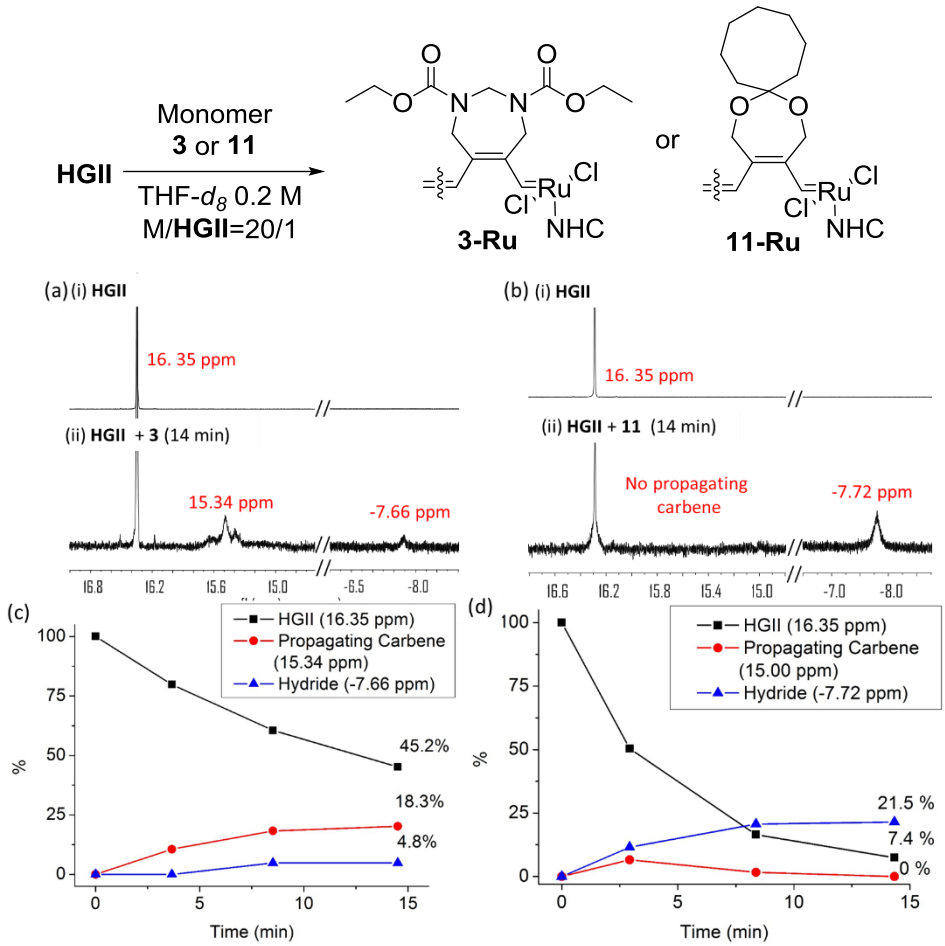


Figure 6. ^{1}H NMR spectra of the propagating carbenes and Ru hydrides during the reactions with (a) aminal **3** with **HGII**, (b) acetal **11** with **HGII**, and (c – d) their respective kinetic plots over time.

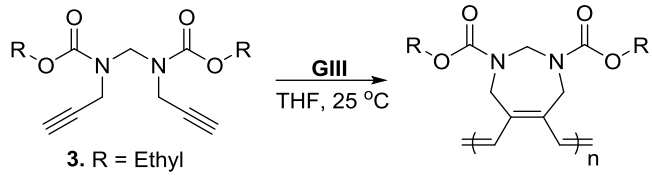
increased in intensity to 18 and 5%, respectively, after 14 min (Figures 3.6a and 3.6c). In contrast, after 14 min of the CP of acetal **11**, the propagating carbene signal at 15.0 ppm completely disappeared, and the intensity of the RuH peak at −7.7 ppm increased to 22% (Figures 3.6b and 3.6d). To confirm

that RuH was produced during CP of the monomers, under the identical condition, we added 4 eq. of 2,6-dichloro-1,4-benzoquinone, which is known to quench RuH during olefin metathesis reactions,[17b] and the peak at −7.7 ppm decreased in intensity from 22 to 3% (Figure S3).[18] From these results, we could explain that, despite their faster cyclization, the less stable 14e$^-$−Ru propagating carbenes from the acetal monomers were easily decomposed to RuH, while those from the aminal monomers were more stable, thereby producing less RuH presumably due to steric bulkiness of the carbamate group retarding the bimolecular decomposition pathway[17b,c,19] (Scheme 3.3).

3.3.3 Controlled Polymerization

Based on the kinetic results and the carbene stability test, we attempted the controlled CP of aminal monomers using the fast-initiating **GIII** (Table 3). Fortunately, the molecular weights of poly(**3**) were directly proportional to the M/I (from 4.1 to 9.4 kDa with M/I from 10/1 to 30/1) and their polydispersity indices (PDIs) were fairly narrow (Table 3.3, entries 1−3, Figure 3.7a, and Figure S5a). Monomer **4** also underwent controlled polymerization to give a linear increase in M_n up to 16.1 kDa upon changing

Table 3.3 Controlled polymerization of monomers **3** and **4** using **GIII**



3. R = Ethyl
4. R = *iso*-Propyl

Entry	Monomer	[M]/[I]	Conv. (M)	Time (h)	Mn (kDa)[a]	PDI[a]	Conv. (%)[b]	Yield (%)[c]
1	**3**	10	0.03	3	4.1	1.19	99	92
2	**3**	20	0.03	4	7.3	1.18	98	81
3	**3**	30	0.03	7	9.4	1.37	99	92
4	**4**	10	0.06	3.5	4.8	1.18	99	61
5	**4**	20	0.06	5	8.7	1.16	98	71
6	**4**	30	0.06	9	11.1	1.25	99	78
7	**4**	40	0.06	12	16.1	1.29	99	72

[a] Determined by chloroform SEC calibrated using polystyrene (PS) standards. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yield after purification.

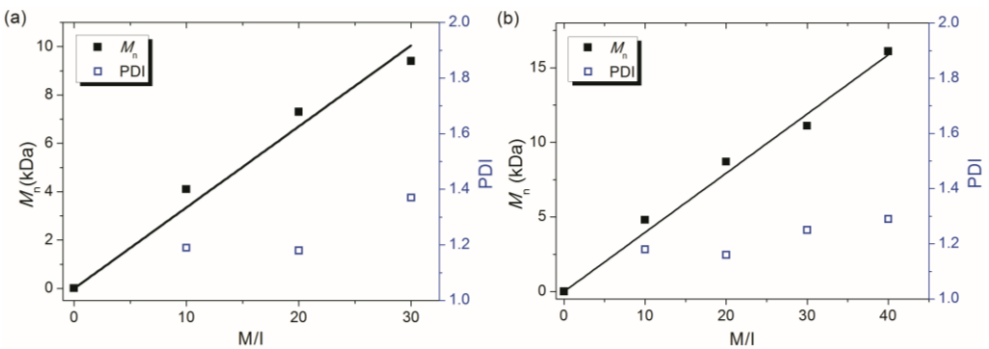


Figure 7. Plots of M_n vs. M/I and corresponding PDI values for (a) poly(**3**), and (b) poly(**4**).

the M/I from 10/1 to 40/1 and narrow PDI<1.3 (Table 3.3, entries 4–7, Figure 3.7b, and Figure S5b). Better controlled polymerization and a narrow PDI using monomer **4** is consistent with the results of our previous carbene stability experiment (Figure 3b). Although overall carbene stability in the CP of 1,8–nonadiynes was relatively lower than that of 1,6–heptadiynes or 1,7–octadiynes, a controlled polymerization was successfully achieved from these challenging monomers.

With the successful controlled CP of monomer **4** in hand, we could synthesize various block copolymers composed of different ring sizes on each block (Figure 3.8a). Poly(**14**)$_{20}$ containing five–membered rings exclusively was initially synthesized by living CP using **GIII**. Subsequently, 20 eq. of 1,8–nonadiyne monomer **4** was added to complete the synthesis of poly(**14**)$_{20}$–*b*–poly(**4**)$_{20}$, which contained blocks of five–membered carbocycles and seven–membered heterocycles. The microstructure of poly(**14**)$_{20}$–*b*–poly(**4**)$_{20}$ was verified by size–exclusion chromatography (SEC), showing a complete shift of the trace from 6.5 kDa to 13.3 kDa with a narrow PDI (1.24) (Figure 3.9a). We also achieved the synthesis of a triblock copolymer, in which blocks of five–, six–, and seven–membered rings were sequentially connected (Figure 8b). Likewise, the most reactive 1,6–heptadiyne monomer **15** was first

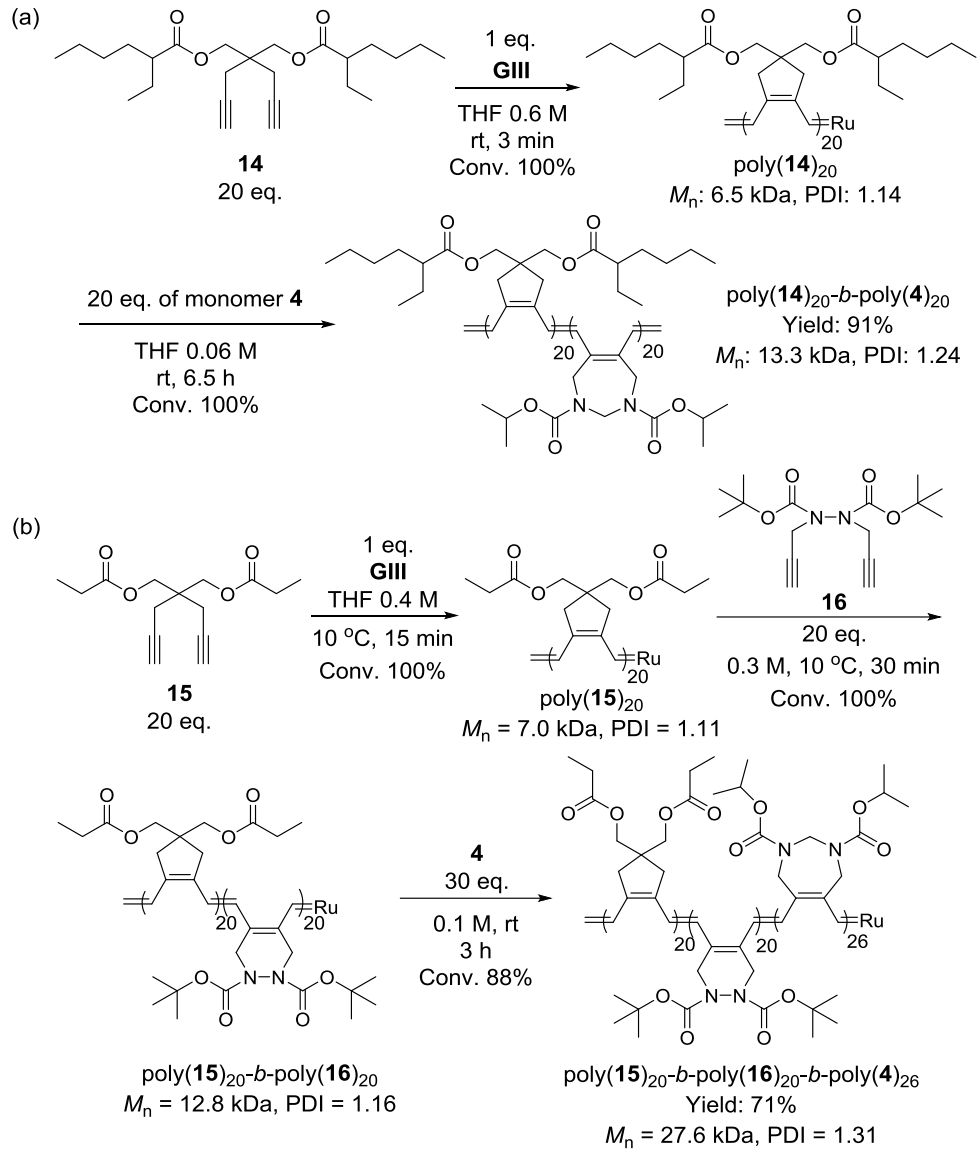


Figure 3.8 (a) Diblock copolymerization of monomers **13** and **4**, (b) triblock copolymerization of monomers **14**, **15**, and **4**.

polymerized to produce the five-membered ring-containing poly(**15**)$_{20}$, followed by the sequential addition of 1,7-octadiyne **16** and 1,8-nonadiyne **4** to give poly(**15**)$_{20}$-*b*-poly(**16**)$_{20}$-*b*-poly(**4**)$_{26}$, which is the first example of a triblock copolymer containing five-, six-, and seven-membered rings. The microstructure of poly(**15**)$_{20}$-*b*-poly(**16**)$_{20}$-*b*-poly(**4**)$_{26}$ was verified by the same way, with a complete shift of the SEC trace from 7.0 kDa to 12.8 kDa and finally to 27.6 kDa being observed, while maintaining a narrow PDI (1.31) (Figure 3.9b). This work highlights the great utility of living CP using **GIII** to produce various polyenes having specific control over the precise ring sizes.

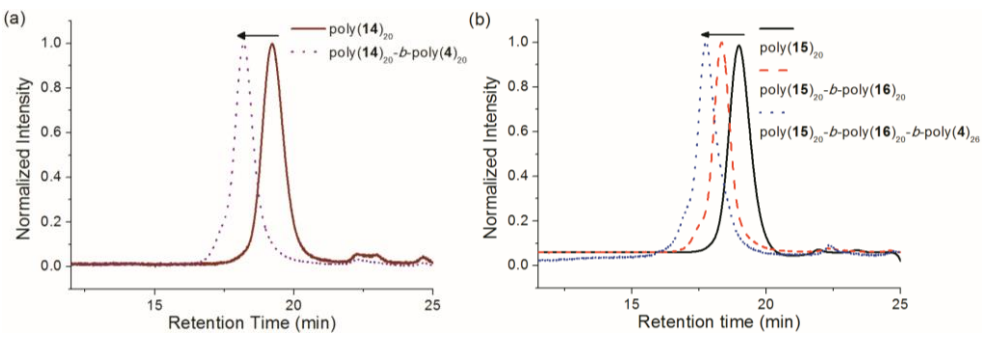


Figure 3.9 SEC traces of (a) diblock copolymer poly(**14**)$_{20}$-*b*-poly(**4**)$_{20}$ and (b) triblock copolymer poly(**15**)$_{20}$-*b*-block(**16**)$_{20}$-*b*-block(**4**)$_{26}$.

3.3.4 Optoelectronic Properties

The prepared conjugated polyenes containing seven-membered N- or O-heterocycles were then analyzed by UV-Vis spectroscopy. We used polymers exhibiting a similar degree of polymerization (DP = 30) for comparison. In chloroform, the band gaps and λ_{max} for the aminal polymers (poly(**3**)-poly(**6**)) were in the range of 2.0 – 2.1 eV and 487 – 508 nm, respectively (Figure 3.10a), whereas the corresponding values for the acetal polymers (poly(**8**)-poly(**12**)) were blue-shifted to 2.1 – 2.2 eV and 444 – 462 nm (Figure 3.10b). A similar blue-shift of λ_{max} was observed in thin films, with values of 495 – 515 and 441 – 460 nm being observed for the aminal and acetal polymers, respectively (Figure S6), indicating that the aminal polymers had a longer effective conjugation length and a higher coplanarity on the polymer backbone than the acetal polymers. This was presumably because of the wider N-C-N bond angle (107.8°) compared to that of O-C-O (104.5°). Upon increasing the molecular weight, the λ_{max}s of poly(**3**)-poly(**5**) remained constant, while the λ_{max} of poly(**6**) increased by 56 nm in chloroform (from 507 to 563 nm) and by 55 nm in the thin film (from 515 to 570 nm), and the band gap decreased by 0.2 eV (Figure S6) presumably due to the benzyl group exhibiting some positive effect on the coplanarity of the backbone. In short,

we could confirm that the λ_{max} of cycloheptyl polyenes is generally smaller than that of cyclopentyl polyenes (480 – 600 nm),[20,21] but is similar to that of cyclohexyl polyenes (440 – 513 nm).[12] These results indicate that conformation of the aminal polymers have less coplanarity than cyclopentyl polyenes but similar coplanarity to cyclohexyl polyenes. We compared the stoke shift of poly(**4**) with those of cyclopentyl polyene (poly(dihexyldipropargyl malonate), poly(DHDPM)) and cyclohexyl polyene (*tert*–butyl hydrazide, poly(**6**) in chapeter 2) (Figure 3.11). Large stoke–shift (153 nm) was observed in poly(**4**) compared to the other polymers, implying that less rigidity than poly(DHDPM) and hydrazide–containing poly(**6**). We also measured the highest occupied molecular orbital (HOMO) levels of poly(**4**) and poly(**12**) by cyclic voltammetry (CV) in dichloromethane and obtained values of −4.90 and −4.98 eV, respectively (Figure S7).

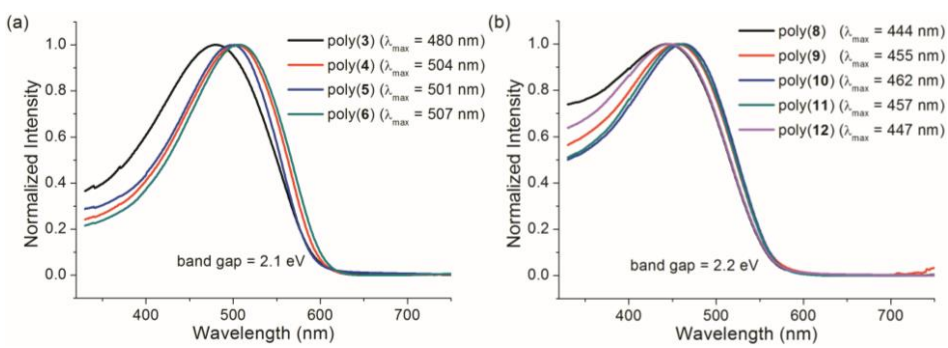


Figure 3.10 Absorption spectra of (a) poly(aminal)s and (b) poly(acetal)s in 0.01 mg/mL chloroform solution.

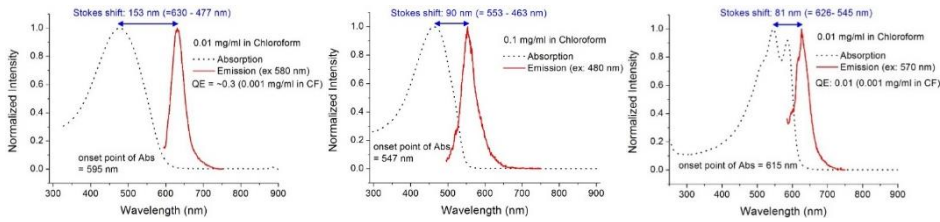


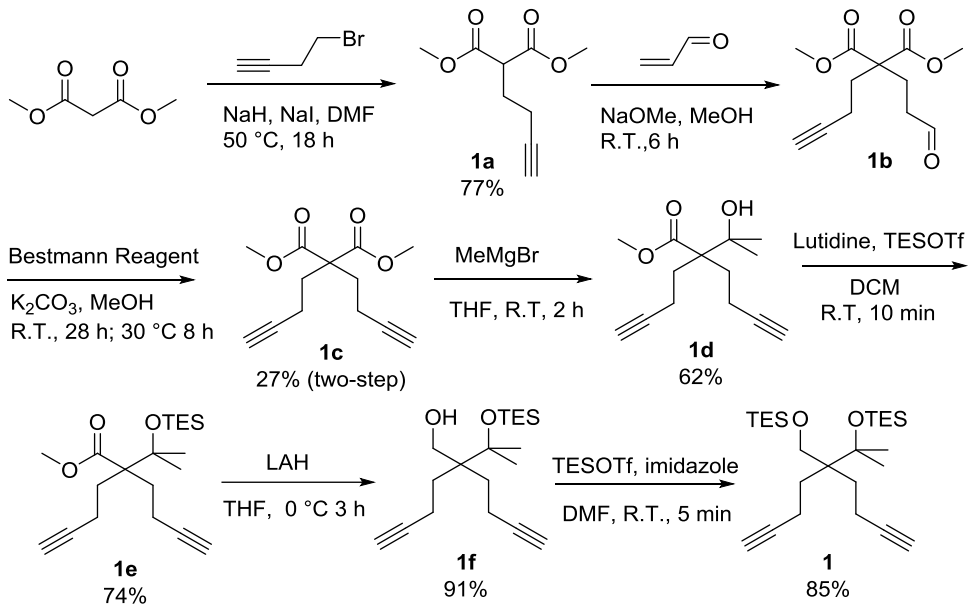
Figure 3.11. Emission spectra of (a) poly(**4**) (b) poly(**6**) in Ch.2 and (c) poly(DHDPM)

3.3 Conclusion

In conclusion, we synthesized the new class of conjugated polyenes containing seven-membered heterocycles, for the first time, by the CP of 1,8-nonadiynes via α-addition of Grubbs catalysts. Despite the difficulties of constructing this medium-sized ring, its synthesis was successfully achieved through the novel design of monomers where heteroatoms were introduced at specific positions as aminal and acetal groups to benefit from their short bond lengths and low rotational barriers. Through the extensive mechanistic investigation, we realized that the CP of 1,8-nonadiynes was difficult because the challenging cyclization step was RDS. Especially, we could observe both the active $14e^{-}$-Ru propagating carbene and decomposition of the catalyst to RuH by ^{1}H NMR. In addition, comparison of the two types of monomers revealed that k_p was larger for the CP of the acetal monomers, but the overall efficiency of the CP of the aminal monomers was higher because the carbene

stability was higher due to the steric bulkiness of the carbamate group in the aminal monomers retarding the decomposition to RuH. Finally, we achieved the controlled CP of these reactive aminal monomers using GIII and the synthesis of a triblock copolymer containing five-, six-, and seven-membered rings as well. This work not only expanded the structural diversity of conjugated polyenes prepared by the CP of diynes, but also provided deep insightful understanding into the mechanism of olefin metathesis polymerizations.

3.5 Experimental Section and Supporting Information



Scheme S1. Synthesis of Carbon Monomer **1**

1a: Di-methyl malonate (1 g, 7.57 mmol) is added to the Ar-purged flask in DMF (12 ml). Solution was cooled to 0 ℃ and sodium hydride (60% in mineral oil, 3.56 mmol, 0.14 mg) was added. After stirring for 15 min at room temperature, 1-bromo-4-butyne (0.47 g, 3.56 mmol) and NaI (0.53 g, 3.56 mmol) were added to the reaction mixture. After stirring for 18 h at 50℃, cool down the solution to rt. The mixture was quenched by aqueous NH_4Cl solution. Product was extracted with ethyl acetate and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated

to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane=1:10) to afford the compound **1a** (0.50 mg, 2.74 mmol, 77 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 6H, OC*H*$_3$), 3.62 (t, *J* = 7.4 Hz, 1H, COC*H*CO), 2.41 – 2.26 (m, 2H, C*H*$_2$C), 2.19 – 2.09 (m, 2H, CHC*H*$_2$), 2.00 (t, *J* = 1.5 Hz, 1H, CC*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.55, 82.44, 69.91, 52.78, 50.33, 27.70, 16.69; HR-MS (ESI) $[M+Na]^+$ calcd. for $C_9H_{12}O_4$, 207. 0634, found, 207. 0628.

1b: Acrolein (0.15 g, 2.74 mmol) was added to the **1a** solution in MeOH then, NaOMe (29.6 mg, 0.55 mmol) was added to the mixture. After stirring for 6 h, evaporate the solution to remove MeOH. Product was extracted with diethyl either and the organic layer was washed with Brine. The organic layer was dried with MgSO4 and concentrated to give a yellow colored liquid. Without further purification, it was used for the next step.

1c: K_2CO_3 (0.76 g, 5.48 mmol) and Bestmann reagent (0.8 ml, 3.29 mmol) were added to the **1b** (0.66 g, 2.74 mmol) solution in MeOH (39 ml). After stirring for 12 h, the reaction was quenched by aqeous $NaHCO_3$ solution. Product was extracted with diethyl ether and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on

silica gel (EtOAc:Hexane=1:5) to afford the compound **1c** (0.17 g, 0.74 mmol, two-step: 27%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.71 (s, 6H, OCH_3), 2.21 – 2.05 (m, 8H, CHCH_2CH_2), 1.95 (t, J = 2.2 Hz, 2H, CCH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.02, 82.93, 69.08, 56.58, 52.69, 31.74, 14.11; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{13}H_{16}O_4$, 259.0947, found, 259.0942.

1d-1f and **1** were synthesized by slightly modifying our previously reported monomer synthetic method[23]. Strong base, 2,6- lutidine (instead of imidazole) and better leaving group, triflate (OTf) (instead of chloride (Cl)) were used, otherwise other conditions were same.

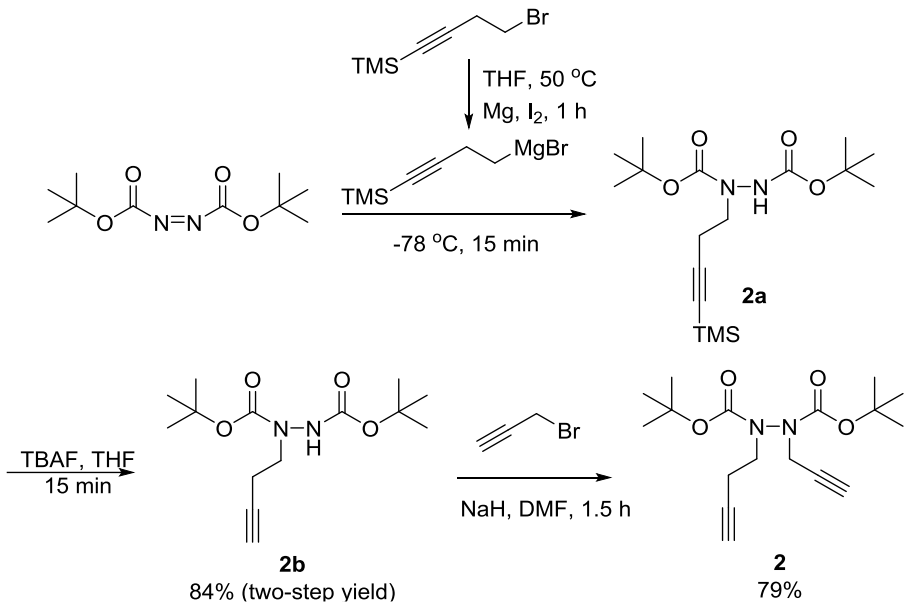
1d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.70 (s, 3H, OCH_3), 2.99 (s, 1H, OH), 2.35 – 2.22 (m, 4H, CH_2CH_2C), 2.15 – 2.01 (m, 2H, CCH_2CH_2), 2.01 – 1.78 (m, 4H, CCH_2CH_2+CCH), 1.21 (s, 6H, C(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.83, 84.21, 74.56, 68.78, 55.86, 52.04, 52.00, 31.62, 26.79, 15.40; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{14}H_{20}O_3$, 259.1310, found, 259.1307.

1e: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.68 – 3.63 (s, 3H, OCH_3), 2.38 (m, 2H, CH_2CH_2C), 2.23 – 2.13 (m, 2H, C$H_2$$CH_2$C), 2.09 – 1.93 (m, 6H, CH_2CH_2C+CCH), 1.30 (s, 6H, C(CH_3)$_2$), 0.99 – 0.91 (t, J = 10 Hz, 9H, Si(CH_2CH_3)$_3$), 0.65 – 0.56 (dd, J = 15, 5 Hz, 6H, Si(C$H_2$$CH_3$)$_3$); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 174.73, 84.87, 77.84, 68.34, 57.23, 51.69, 30.80, 27.73, 15.07, 7.20, 6.87; HR-MS (ESI) $[M+Na]^+$ calcd. for $C_{20}H_{34}O_3Si$, 373.2175, found, 373.2166.

1f: ^1H NMR (500 MHz, $CDCl_3$) δ 3.59 (d, J = 5.0 Hz, 2H, CH_2OH), 3.53 (t, J = 5.2 Hz, 1H, OH), 2.39 – 2.28 (m, 2H, CH_2CH_2C), 2.27 – 2.17 (m, 2H, CH_2CH_2C), 1.98 – 1.94 (t, J = 2.2 Hz, 2H, CCH), 1.79 (m, 2H, CH_2CH_2C), 1.61 (m, 2H, CH_2CH_2C), 1.30 (s, 6H, $C(CH_3)_2$), 0.97 (t, J = 10 Hz, 9H, $Si(CH_2CH_3)_3$), 0.65 (dd, J = 15, 5 Hz, 6H, $Si(CH_2CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 85.00, 81.77, 68.47, 65.57, 45.91, 31.07, 26.66, 14.56, 7.11, 6.85; HR-MS (ESI) $[M+Na]^+$ calcd. for $C_{19}H_{34}O_2Si$, 345.2226, found, 345.2222.

1: ^1H NMR (500 MHz, $CDCl_3$ δ 3.53 (s, 2H, OCH_2), 2.39 – 2.22 (m, 4H, CH_2CH_2C), 1.92 ((t, J = 2.2 Hz, 2H, CCH), 1.81 – 1.70 (m, 2H, CH_2CH_2C), 1.65 (m, 2H, CH_2CH_2C), 1.24 (s, 6H, $C(CH_3)_2$), 1.00 – 0.92 (t, J = 10 Hz, 9H, $Si(CH_2CH_3)_3$), 0.64 – 0.54 (dd, J = 15, 5 Hz, 6H, $Si(CH_2CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 86.01, 78.86, 67.71, 65.72, 46.97, 31.47, 27.41, 14.62, 7.31, 7.01, 4.40; HR-MS (ESI) $[M+Na]^+$ calcd. for $C_{25}H_{48}O_2Si_2$, 459.3093, found, 459.3085.



Scheme S2. Synthesis of Hydrazine Monomer 2

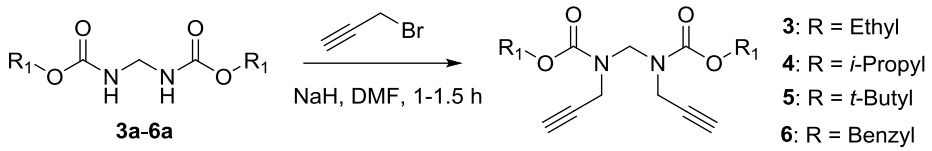
2a: In-situ generated TMS-protected butynyl magnesium bromide from (4-bromo-1-butyn-1-yl)trimethylsilane (1.07 g, 5.21 mmol) was added to the di-*tert*-butyl azodicarboxylate (1g, 4.34 mmol) solution in THF at -78 °C by cannula transfer. After stirring for 15 min, the reaction mixture was allowed to warm to rt. After the reaction mixture was quenched by water, the product was extracted with DCM and the organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated. Without further purification, it was used for the next step.

2b: Tetrabutylammonium fluoride in 1.0 M THF solution (6.51 ml 6.51 mmol)

was added to the **2a** (1.55g, 4.34 mmol) solution in THF (14 ml). After stirring for 15 min, reaction was quenched with water. The product was extracted with ethyl acetate and was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated. The product was purified by column chromatography (EtOAc:Hexane=1:3) to afford the product **2b** (1.04g, 3.65 mmol, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.41 (s, 0.5H, N*H*), 6.13 (s, 0.5H, N*H*), 3.65 (s, 2H, NCH_2), 2.50 (br m, 2H, CH_2C), 1.95 (s, 1H, CC*H*), 1.49 (s, 18H, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.08, 81.43, 69.73, 49.60, 48.67, 28.33, 28.06, 17.84; HR-MS (ESI) $[M+Na]^+$ calcd. for $C_{14}H_{24}N_2O_4$, 307.1634, found, 307.1630.

2: **2b** (1.04g, 3.65 mmol) was dissolved in DMF (18 ml). NaH (60% in mineral oil, 0.15 g, 3.65 mmol) was added to the solution. After stirring for 15 min at 0 ℃, propargyl bromide (80wt% in toluene, 0.6 ml, 4.02 mmol) was added to the solution. The reaction was warm to rt and stirred for 1.5 h. The reaction was quenched with water and the product was extracted with diethyl ether. The organic layer was washed with brine, dried with $MgSO_4$ and concentrated. The product was purified with by column chromatography (EtOAc:Hexane=1:5) to afford the product **2** (0.93g, 2.88 mmol, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.64 – 4.27 (m, 1.5H, NCH_2C), 4.00 – 3.85

(m, 0.5H, NCH_2C), 3.75 – 3.47 (m, 2H, NCH_2CH$_2$), 2.62 – 2.46 (m, 2H, NCH$_2$CH_2), 2.25 (t, J = 2.5 Hz, 1H, CCH), 1.94 (t, J = 2.6 Hz, 1H, CCH), 1.51 – 1.37 (m, 18H, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.14, 82.00, 81.68, 81.52, 78.45, 77.42, 77.16, 76.91, 73.04, 69.60, 50.71, 49.32, 39.50, 39.35, 28.27, 28.24, 28.14, 18.42, 18.01; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{17}H_{26}N_2O_4$, 345.1791, found, 345.1789.



Scheme S3. Synthesis of Aminal Monomers **3**–**6**.

3a–**6a** were prepared according to the literature and their spectroscopic data were reported in the same literature except **5a**.[22]

5a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 (br s, 2H, NHCH$_2$NH), 4.37 (br s, 2H, NHCH_2NH), 1.39 (m, 18H, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.17, 79.85, 47.51, 28.42; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{11}H_{22}N_2O_4$, 269.1478, found, 269.1473.

3–**6**: Aminal compound (**3a**–**6a**, 3.00 mmol) was dissolved in the DMF (7.5 ml). Propargyl bromide (80wt% in toluene, 1.12 ml, 7.5 mmol) was first added to the aminal solution then, NaH (60% in mineral oil, 0.26 g, 6.6 mmol)

was added. After stirring for 1.5 h, the reaction was quenched with water and the product was extracted with diethyl ether. The organic layer was washed with brine and dried with MgSO4. The organic layer was concentrated and the product was purified by column chromatography (EtOAc:Hexane=1:10 → EtOAc:Hexane=1:3) to afford the product. In the ^{1}H and ^{13}C NMR spectra, we observed broad and multiple signals due to rotational isomers.

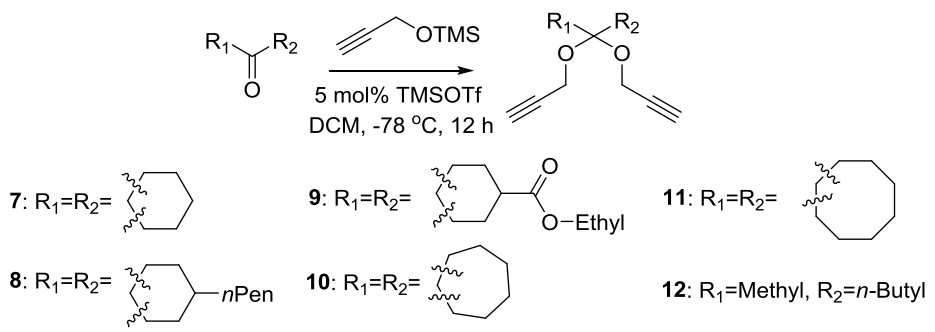
3: 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.97 (br s,2H, NCH_2N), 4.10 (dd, J = 14.2, 7.0 Hz, 4H, OCH_2CH$_3$), 4.00 (br s, 4H, NCH_2C), 2.13 (br s, 2H, CCH), 1.19 (br s, J = 4.8 Hz, 6H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.09, 155.76, 155.17, 79.38, 79.04, 71.28, 71.04, 62.05, 58.23, 57.45, 56.71, 35.67, 35.01, 14.40; HR-MS (ESI) [M+Na]$^+$ calcd. for $C_{13}H_{18}N_2O_4$, 289.1165, found, 289.1157.

4: 68% yield. ^{1}H NMR 500 MHz, $CDCl_3$) δ 5.04 (br s, 2H, CH(CH$_3$)$_2$), 4.96 (br s, 2H, NCH_2N), 4.04 (br s, 4H, NCH_2C), 2.17 (br s, 2H, CCH), 1.26 (br s, 12H, CH(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.01, 155.64, 154.96, 79.73, 79.44, 70.99, 69.95, 58.29, 57.27, 56.38, 35.85, 34.87, 22.14; HR-MS (ESI) [M+Na]$^+$ calcd. for $C_{15}H_{22}N_2O_4$, 317.1478, found, 317. 1473.

5: 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.93 (br s, 2H, NCH_2N), 4.00 (br s, 4H, NCH_2C), 2.12 (br s, 2H, CCH), 1.53 – 1.35 (br s, 18H, C(CH_3)

$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.37, 154.93, 154.30, 81.48, 81.00, 79.70, 70.76, 57.18, 36.18, 35.23, 34.17, 28.31; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{17}H_{26}N_2O_4$, 345.1791, found, 345.1784.

6: 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.24 (br m, 10H, Ph), 5.20 – 5.10 (m, 4H, PhC*H*$_2$O), 5.09 (br s, 2H, NC*H*$_2$N), 4.14 (br s, 2H, NC*H*$_2$C), 4.01 (d, *J* = 30.1 Hz, 2H, NC*H*$_2$C), 2.15 (s, 2H, CC*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.97, 155.61, 154.98, 136.09, 135.70, 128.39, 128.02, 127.70, 79.23, 71.66, 71.36, 67.98, 67.62, 58.74, 57.79, 57.01, 35.94, 35.20; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{23}H_{22}N_2O_4$, 413.1478, found, 413.1470.



Scheme S4. Synthesis of Aminal Monomers **7**–**12**.

7–**12** were synthesized by the same method in the literature.[23] We used 2.5 equiv (propargyloxy)trimethylsilane and the product was purified by column chromatography (EtOAc:Hexane=1:50).

7: 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.13 (d, *J* = 2.5 Hz, 4H, OC*H*$_2$),

2.38 (t, J = 2.5 Hz, 2H, CCH), 1.70 – 1.65 (m, 4H, CH_2CCH_2), 1.53 (dt, J = 11.9, 6.1 Hz, 4H, CH_2CH$_2$CH_2), 1.38 (dt, J = 11.5, 5.9 Hz, 2H, CH$_2$CH_2CH$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 102.13, 80.72, 73.43, 48.66, 33.50, 25.40, 22.89; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{12}H_{16}O_2$, 215.1048, found, 215.1043.

8: 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.15 (dd, J = 32.6, 2.4 Hz, 4H, OCH_2), 2.39 (dd, J = 5.4, 2.5 Hz, 2H, CCH), 1.97 (d, J = 12.5 Hz, 2H, CyHex), 1.63 (dd, J = 9.1, 3.9 Hz, 2H, CyHex), 1.45 (td, J = 13.3, 3.7 Hz, 2H, CCH_2(CH$_2$)$_3$CH$_3$), 1.34 – 1.10 (m, 11H, CH$_2$C$_2$$H_4CH_3$+CyHex), 0.87 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 102.43, 80.89, 80.65, 73.46, 48.86, 48.78, 36.69, 36.25, 33.00, 32.26, 29.20, 26.97, 22.79, 14.22; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{17}H_{26}O_2$, 285.1831, found, 285.1826.

9: 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.08 (t, J = 6.2 Hz, 2H, OCH_2CH$_3$), 4.07 – 4.00 (m, 4H, OCH_2C), 2.33 (t, J = 2.1 Hz, 2H, CCH), 2.24 (tt, J = 10.5, 3.9 Hz, 1H, CH$_2$CHCH$_2$), 1.91 (d, J = 13.4 Hz, 2H, CyHex), 1.83 – 1.75 (m, 2H, CyHex), 1.67 (td, J = 13.9, 3.4 Hz, 2H, CyHex), 1.51 – 1.41 (m, 2H, CyHex), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.04, 101.38, 80.56, 80.31, 73.69, 73.65, 60.41, 48.91, 48.82, 41.69, 32.12, 25.17, 14.31; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{15}H_{20}O_4$,

287.1260, found, 287.1254.

10: 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.11 (d, J = 2.5 Hz, 4H, OCH_2C), 2.37 (t, J = 2.5 Hz, 2H, CCH), 1.89 – 1.80 (m, 4H, CyHep), 1.58 – 1.47 (m, 8H, CyHep); ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.57, 80.75, 73.36, 49.05, 36.70, 29.25, 21.83; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{13}H_{18}O_2$, 229.1205, found, 229.1198.

11: 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12 – 4.08 (m, 4H, OCH_2C), 2.39 – 2.35 (m, 2H, CCH), 1.81 (s, 4H, CyOct), 1.54 (s, 10H, CyOct); ^{13}C NMR (125 MHz, $CDCl_3$) δ 105.97, 80.74, 73.38, 48.94, 31.11, 28.13, 24.66, 21.60; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{14}H_{20}O_2$, 243.1361, found, 243.1354.

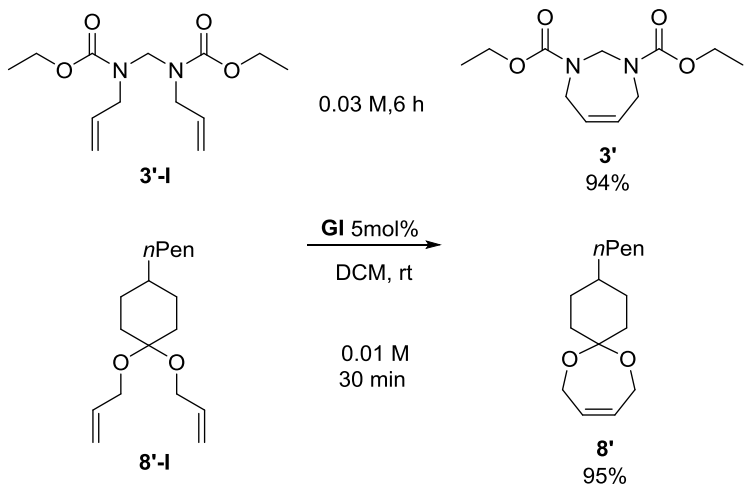
12: 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.16 – 4.07 (m, 4H, OCH_2), 2.37 (t, J = 2.5 Hz, 2H, CCH), 1.65 – 1.59 (m, 2H, CCH_2CH$_2$), 1.37 – 1.24 (m, 7H, CH_2CH_2CH_3), 0.89 (m, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 103.69, 80.60, 73.44, 49.23, 49.21, 36.92, 26.39, 22.93, 21.87, 14.06; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{12}H_{18}O_2$, 217.1205, found, 217.1198.

13 were prepared by the same method for the synthesis of aminal monomer **3** except the equivalent of propargyl bromide (0.9 eq. to **3a**) and NaH (1.0 eq. to **3a**). 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (s, 0.5H, NH), 5.48

(s, 0.5H, N*H*), 4.77 (s, 2H, NCH_2C), 4.20 (m, 6H, NCH_2N+OCH_2), 2.24 (s, 1H, CC*H*), 1.29 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.05, 156.65, 156.03, 155.43, 79.53, 71.37, 62.14, 61.24, 53.90, 53.18, 36.77, 29.73, 29.40, 14.61; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{10}H_{16}N_2O_4$, 251.1008, found, 251.1003.

14-**16** were prepared according to the literature and their spectroscopic data were reported in the same literature except **14**.[12d,21]

14: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.08 (s, 4H, OCH_2), 2.38 (d, J = 2.7 Hz, 4H, CH_2CCH), 2.26 (tt, J = 8.8, 5.4 Hz, 2H, CH_2C*H*CH_2), 2.01 (t, J = 2.6 Hz, 2H, CC*H*), 1.64 – 1.53 (m, 4H, , CHC$H_2$$CH_3$), 1.53 – 1.38 (m, 4H, CHC$H_2$$CH_2$), 1.30 – 1.14 (m, 8H, $C_2H_4CH_3$), 0.85 (td, J = 7.4, 4.2 Hz, 12H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.83, 78.77, 71.75, 64.64, 47.47, 40.10, 31.82, 29.64, 25.56, 22.70, 22.17, 13.98, 11.89; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{25}H_{40}O_4$, 427.2825, found, 427.2813.



Scheme S5. Synthesis of Model Compounds **3'** and **8'** by Ring-Closing Metathesis

Procedure for **3'-I** (75%) and **8'-I** (65%) synthesis is identical as mentioned above but propargyl was changed to allyl reagent.

3'-I: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (s, 2H, CH_2CHCH_2), 5.10 (br m, 4H, CH_2CHCH_2), 4.83 (s, 2H, NCH_2N), 4.09 (br m, 4H, OCH_2), 3.82 (br m, 4H, NCH_2CH), 1.27 – 1.12 (m, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.54, 155.61, 128.77, 128.71, 128.08, 61.85, 60.05, 59.82, 44.30, 43.94, 43.88, 14.75, 14.71.; HR-MS (ESI) $[M+Na]^+$ calcd. for $C_{13}H_{22}N_2O_4$, 293.1478, found, 293.1472.

8'-I: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (dtt, J = 22.0, 10.9, 5.5 Hz, 2H, CH_2CHCH_2), 5.26 (ddd, J = 17.1, 14.0, 1.7 Hz, 2H, CH_2CHCH_2), 5.15 – 5.05 (m, 2H, CH_2CHCH_2), 3.93 (dd, J = 41.2, 5.5 Hz, 4H, OCH_2), 1.99 (d, J

= 12.4 Hz, 2H, CyHex), 1.65 – 1.56 (m, 2H, CyHex), 1.39 (td, *J* = 13.3, 3.8 Hz, 2H, CyHex), 1.33 – 1.07 (m, 11H, $C_4H_8CH_3$+CyHex), 0.86 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.57, 135.38, 115.90, 115.77, 100.80, 61.28, 61.06, 36.87, 36.39, 33.26, 32.26, 29.35, 26.97, 22.75, 14.15; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{17}H_{30}O_2$, 289.2144, found, 289.2144.

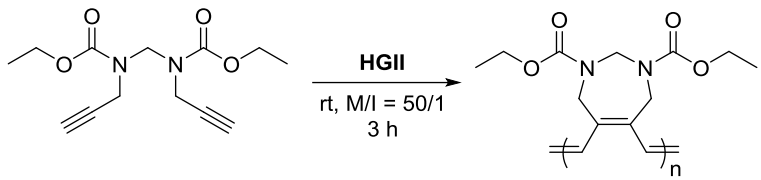
Substrates **3'-I** and **8'-I** (0.5 mmol) were dissolved in DCM (degassed for 15 min with Ar), respectively. Grubbs catalyst 1st generation (GI, 0.025 mmol) was added to the solution. The reaction mixture was stirred and monitored by TLC. After complete consumption of the substrate, the reaction was quenched by EVE. After solvent evaporation, the product was purified by column (EtOAc:Hexane=1:5 for **3'** and EtOAc:Hexane=1:50 for **8'**) to afford the each product.

3': ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 – 5.63 (m, 2H, C*H*C*H*), 5.07 (t, *J* = 18.5 Hz, 2H, NCH_2N), 4.14 (dq, *J* = 14.2, 7.0 Hz, 4H, OCH_2), 3.93 (dd, *J* = 34.3, 10.5 Hz, 4H, NCH_2CH), 1.24 (dd, *J* = 15.1, 7.5 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.54, 156.26, 155.61, 155.45, 128.77, 128.71, 128.08, 61.85, 60.05, 59.82, 44.30, 43.94, 43.88, 14.75, 14.71; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{11}H_{18}N_2O_4$, 265.1165, found, 265.1161.

8': ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 – 5.61 (m, 2H, C*H*C*H*), 4.28 – 4.17 (m, 4H, OCH_2), 2.08 (dd, J = 14.4, 2.5 Hz, 2H, CyHex), 1.66 – 1.58 (m, 2H, CyHex), 1.37 (td, J = 13.3, 4.0 Hz, 2H, CyHex), 1.31 – 1.07 (m, 11H, $C_4H_8CH_3$+CyHex), 0.86 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 129.81, 129.78, 102.30, 60.94, 60.70, 36.98, 36.38, 32.28, 32.20, 29.55, 27.00, 22.78, 14.19; HR-MS (ESI) [**M**+Na]$^+$ calcd. for $C_{15}H_{26}O_2$, 261.1831, found, 261.1826.

General procedure for polymerization: A 4-mL sized screw-cap vial with septum was flame dried and charged with monomer and a magnetic bar. The vial was purged with argon three times, and degassed anhydrous THF was added. After the Ar-purged **HGII** in another 4-mL vial was dissolved in THF, the solution was rapidly injected to the monomer solution at rt under vigorous stirring. The reaction was quenched by excess ethyl vinyl ether after desired reaction time, and concentrated by evaporation. The polymer was purified by precipitation in hexane (aminal polymers) or methanol (acetal polymers) at rt. Obtained polymer was filtered and dried in vacuo. Remaining small amount of crude mixture (<10%) was used for calculating the monomer conversion by ^{1}H NMR.

Table S1. Screening Concentrations



Conc. (M)	Conv. (%)
0.03	67
0.06	60
0.12	59
0.6	26

^{1}H and ^{13}C NMR characterization of polymers

Poly(**3**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 6.00 (m, 2H), 5.09 (s, 2H), 4.41 (s, 4H), 4.08 (s, 4H), 1.22 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.12, 155.00, 141.54, 136.22, 125.46, 61.79, 60.61, 45.41, 14.68.

Poly(**4**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 6.64 (m, 2H), 5.10 (s, 2H), 4.87 (s, 2H), 4.34 (d, J = 80.8 Hz, 4H), 1.17 (d, J = 50.6 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.40, 154.61, 136.41, 125.64, 69.28, 60.24, 44.85, 22.27.

Poly(**5**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 6.17 (m, 2H), 4.99 (s, 2H), 4.29 (s, 4H), 1.63 – 1.10 (m, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.68, 154.16, 135.49, 127.02, 124.86, 80.38, 60.19, 58.88, 44.99, 28.47.

Poly(**6**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 6.41 (m, 12H), 5.01 (s, 6H), 4.70 – 3.78 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.16, 154.65, 141.64, 136.57, 128.60, 127.93, 125.90, 123.25, 60.30, 45.49.

Poly(**8**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (br m, 2H), 4.78 – 4.17 (m, 4H), 2.08 (br s, 2H), 1.58 (br s, 2H), 1.48 – 1.03 (br m, 14H), 0.87 (br m, 3H); ^{13}C NMR (125 MHz, , $CDCl_3$) δ 136.26, 124.98, 102.22, 61.41, 36.99, 36.38, 32.31, 32.02, 29.53, 27.04, 22.83, 14.25.

Poly(**9**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 – 5.91 (br m, 2H), 4.73 – 4.34 (m, 4H), 4.14 (br s, 2H), 2.35 (s, 1H), 2.11 (s, 2H), 1.98 – 1.64 (m, 4H), 1.53 (s, 2H), 1.24 (br s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.20, 136.12, 125.25, 101.20, 61.45, 60.40, 42.06, 31.14, 25.53, 14.38.

Poly(**10**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 – 5.94 (br m, 2H), 4.68 – 3.98 (br m, 4H), 1.93 (br s, 4H), 1.57 (br s, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.19, 125.06, 106.19, 61.77, 35.52, 29.15, 22.38.

Poly(**11**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68 – 5.91 (br m, 2H), 4.65 – 4.01 (br m, 4H), 1.92 (br s, 4H), 1.57 (br s, 10H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 136.16, 125.09, 105.55, 61.47, 30.66, 28.23, 25.09, 22.01.

Poly(**12**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 – 5.71 (br m, 2H), 4.64 – 3.91 (br m, 4H), 1.81 – 1.53 (br s, 2H), 1.37 (br m, 7H), 0.91 (br m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.16, 124.95, 103.57, 61.73, 36.07, 26.72, 23.11, 21.12, 14.18.

Procedures for mechanistic experiments

① 1:1 reaction of 13 and GIII: **GIII** (8.7 mg, 0.011 mmol) and hexamethyldisilane (internal standard, 10 μl) were dissolved in THF-d_8 (0.5 ml). Initial benzylidene was measured by integral ratio of **GIII** to hexamethyldisilane in ^{1}H NMR spectrum. **13** (3 mg, 0.011 mmol) THF-d_8 (60 μl) solution was added to the **GIII** solution and mixed by shaking NMR tube for 10 sec. The reaction was monitored by ^{1}H NMR. After 300 min of the mixing, ethyl vinyl ether (EVE, 0.1 ml) was added to the reaction mixture to quench the reaction and mixed by shaking NMR tube for 10 sec. Fischer carbene was measured by the same method as mentioned above.

② Reaction kinetics: Monomer (0.05 mmol) and hexamethyldisilane (50 μl) were dissolved in THF-d_8 (4.5 ml). Initial monomer was measured by integral ratio of monomer to hexamethyldisilane in ^{1}H NMR spectrum. **HGII** (3.1 mg, 0.005 mmol) THF-d_8 (50 μl) solution was added to the monomer solution

and mixed by shaking NMR tube for 10 sec. The reaction was monitored by ^{1}H NMR for 5 min.

③ Carbene decay: **GIII** (8.0 mg, 0.01 mmol) and hexamethyldisilane (50 μl) were dissolved in THF-d_8 (4.5 ml). Initial benzylidene was measured by integral ratio of **GIII** to hexamethyldisilane in ^{1}H NMR spectrum. Monomer (0.1 mmol) THF-d_8 (50 μl) solution was added to the **GIII** solution and mixed by shaking NMR tube for 10 sec. The propagating carbene was monitored by ^{1}H NMR for 15 min.

④ PyCl addition: Catalyst (0.01 mmol) and hexamethyldisilane (50 μl) were dissolved in THF-d_8 (4.5 ml). Initial benzylidene was measured by integral ratio of catalyst to hexamethyldisilane in ^{1}H NMR spectrum. Monomer (0.1 mmol) THF-d_8 (50 μl) solution was added to the catalyst solution and mixed by shaking NMR tube for 10 sec. The propagating carbene was measured by the same method. 3-Chloropyridine (9.5 μl, 0.1 mmol) was added to the reaction mixture and mixed by shaking NMR tube for 10 sec. The propagating carbene was monitored by ^{1}H NMR. During this experiment, broad signal at 16.6 ppm was observed when PyCl was added (Figure S1). To confirm if this signal comes from **HGII**, we observed the mixture of **HGII** and PyCl by ^{1}H NMR. Complete shift (from 16.3 ppm to 16.6 ppm) was observed.

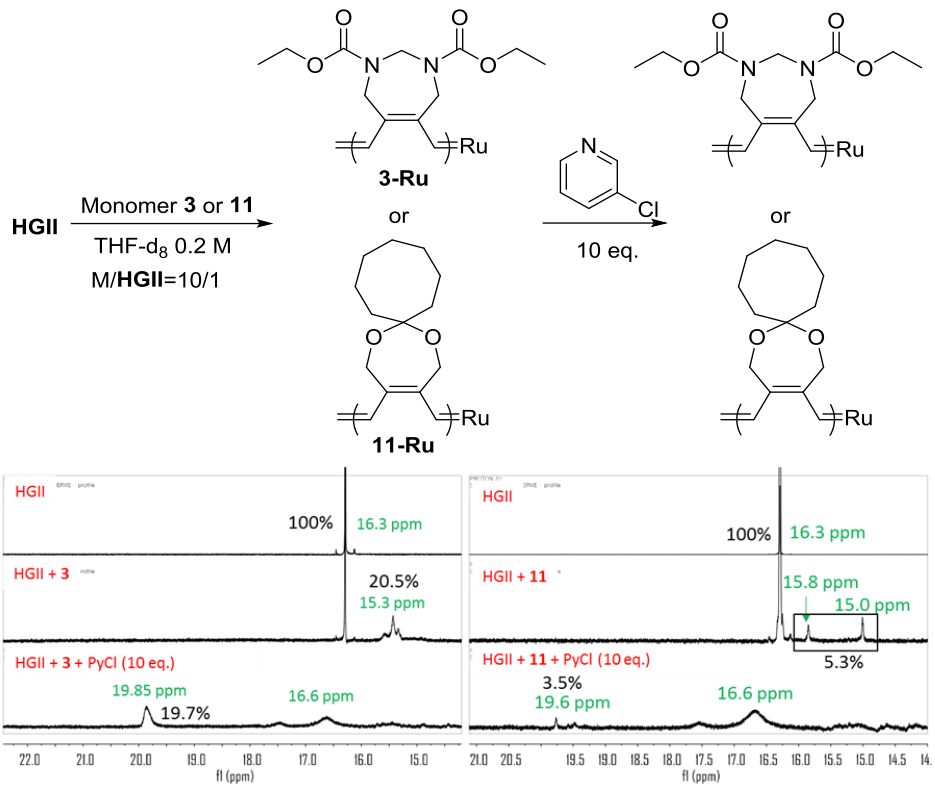


Figure S1. NMR Spectra of Propagating Carbene upon Addition of PyCl

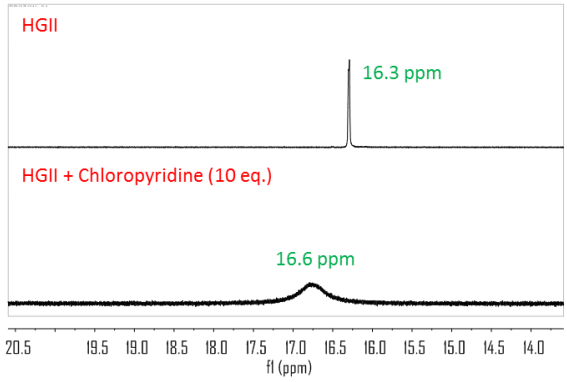


Figure S2. NMR Spectra of HGII and the mixture of HGII and PyCl

⑤ Dynamic equilibrium: **GIII** (8.0 mg, 0.01 mmol) and hexamethyldisilane (50 μl) were dissolved in THF-d_8 (4.5 ml). Initial benzylidene was measured by integral ratio of **GIII** to hexamethyldisilane in ^{1}H NMR spectrum. Aminal **7** (19.23 mg, 0.1 mmol) THF-d_8 (50 μl) solution was added to the **GIII** solution and mixed by shaking NMR tube for 10 sec. The propagating carbene was measured by the same method. ^{1}H NMR was taken whenever 1 equiv. PyCl was added to the solution.

⑥ Hydride observation: **HGII** (6.13 mg, 0.005 mmol) and hexamethyldisilane (50 μl) were dissolved in THF-d_8 (4.5 ml). Initial benzylidene was measured by integral ratio of catalyst to hexamethyldisilane in ^{1}H NMR spectrum. Monomer (0.1 mmol) THF-d_8 (50 μl) solution was added to the catalyst solution and mixed by shaking NMR tube for 10 sec. The propagating carbene was measured by the same method. The propagating carbene and hydride were monitored for 15 min by ^{1}H NMR.

⑦ Addition of 2,6-dichloro-1,4-benzoquinone: HGII (6.13 mg, 0.005 mmol), 2,6-dichloro-1,4-benzoquinone (3.54 mg, 0.02 mmol) and hexamethyldisilane (50 μl) were dissolved in THF-d_8 (4.5 ml). Initial benzylidene was measured by integral ratio of catalyst to hexamethyldisilane in ^{1}H NMR spectrum. Acetal **11** (22.03 mg, 0.1 mmol) THF-d_8 (50 μl) solution was added to the catalyst solution and mixed by shaking NMR tube for 10 sec. The propagating carbene and hydride were monitored for 15 min by ^{1}H NMR.

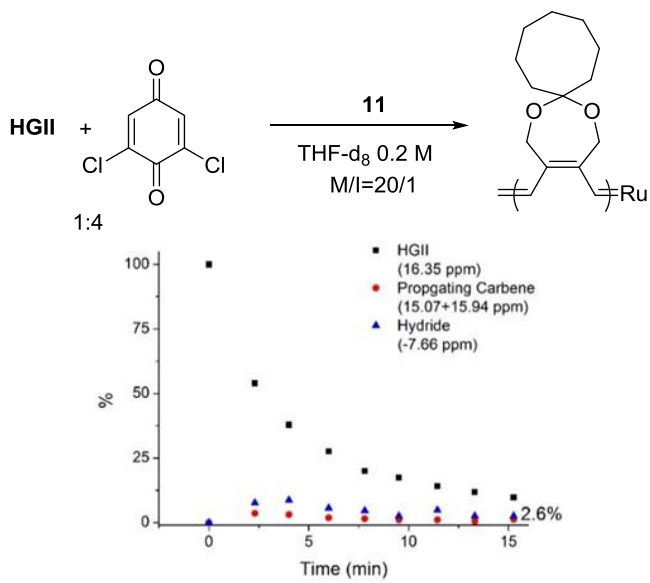


Figure S3. Plot of Hydride and Propagating Carbene over Time

We tried to isolate RuH from the filtrate after purification of polymers but couldn't observe any signals for hydride in ^{1}H NMR spectrum of the filtrate. Instead, we could observe a signal for RuH at 1965.97 cm^{-1} in IR spectrum. Polymerization was carried out by the same procedure for general polymerization. After 10 min, 20 μl of the reaction mixture was taken by a micro-syringe and loaded on the plate then IR spectrum was obtained.

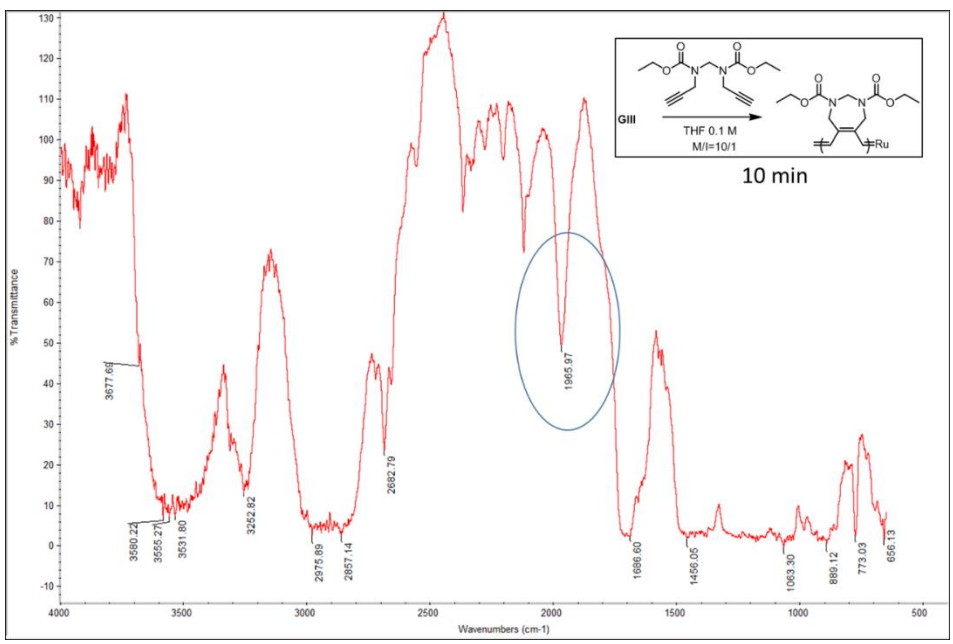


Figure S4. IR spectrum

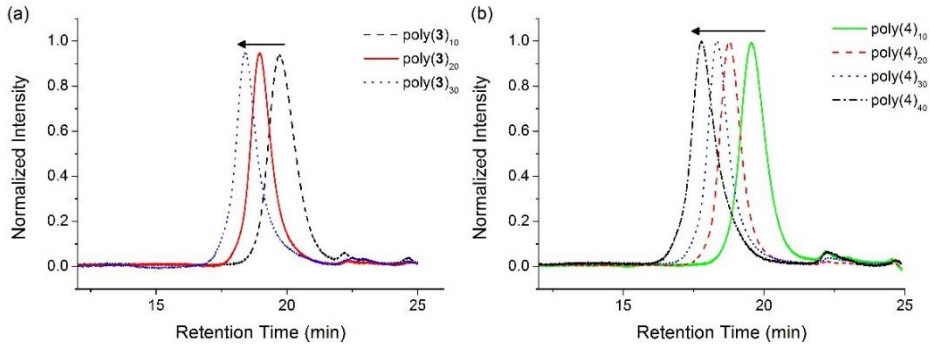
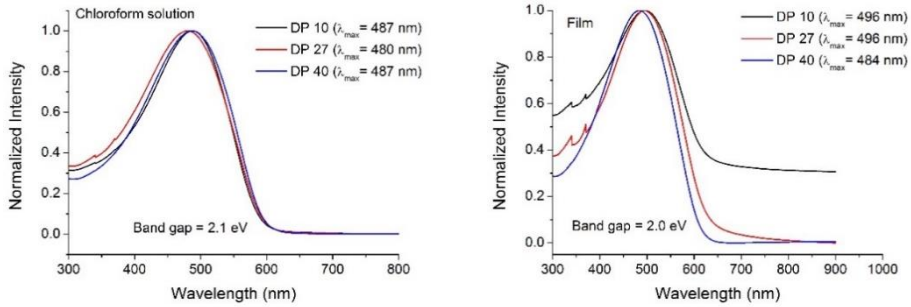


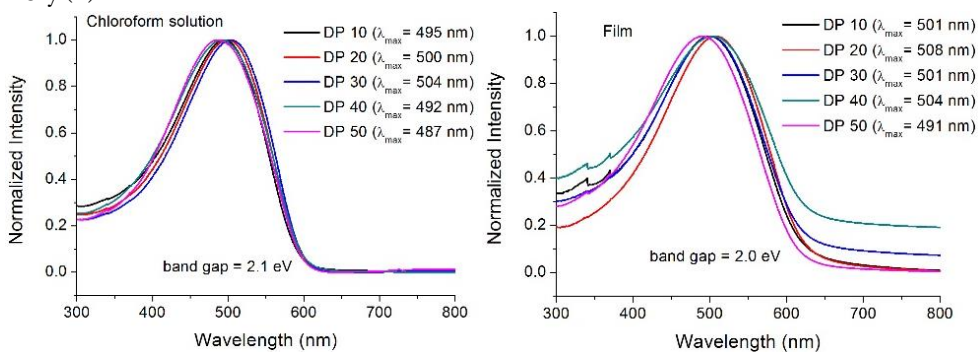
Figure S5. SEC traces of homopolymers obtained from controlled polymerization (in Table 3)

Figure S6. UV/vis absorption spectra

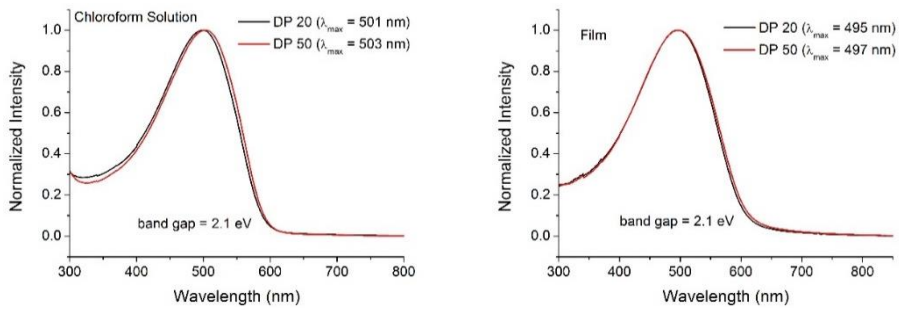
Poly(**3**)



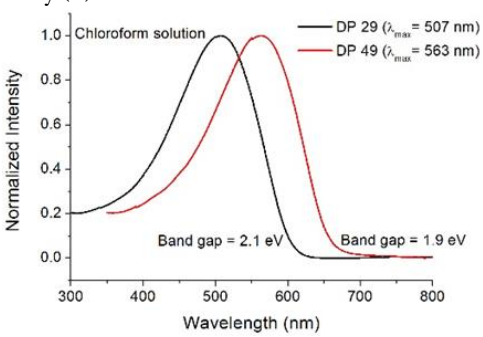
Poly(**4**)

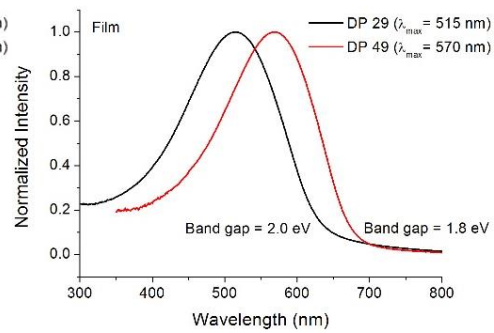


Poly(**5**)

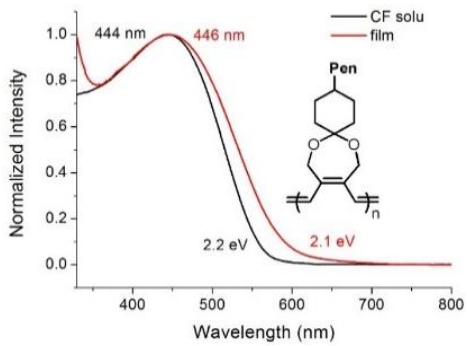


Poly(**6**)

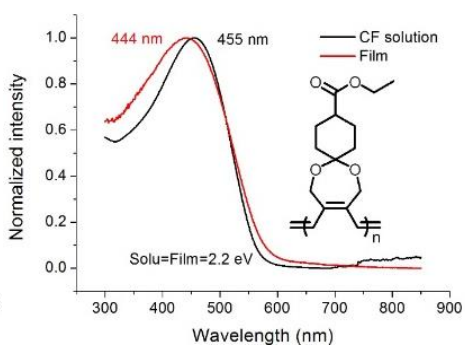




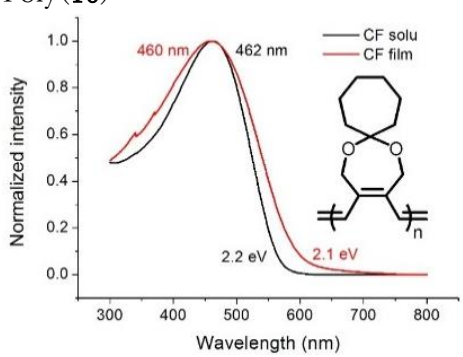
Poly(**8**)



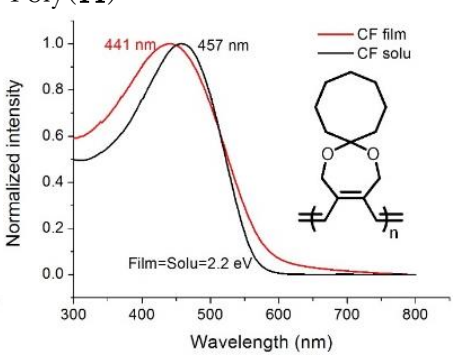
Poly(**9**)



Poly(**10**)



Poly(**11**)



Poly(**12**)

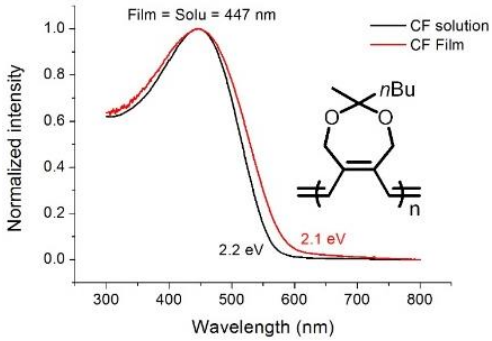


Figure S7. Cyclic voltammograms

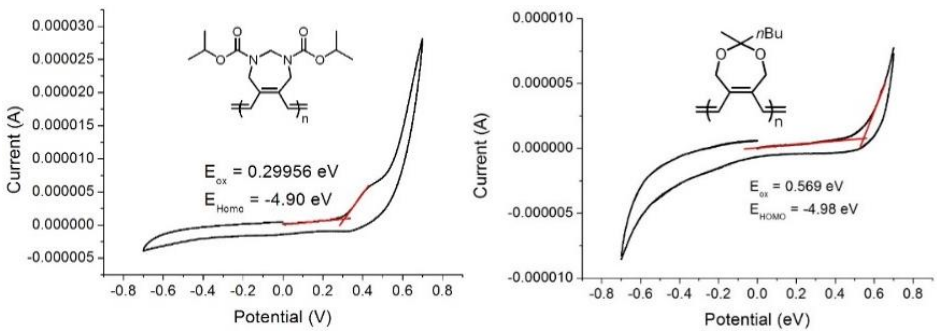
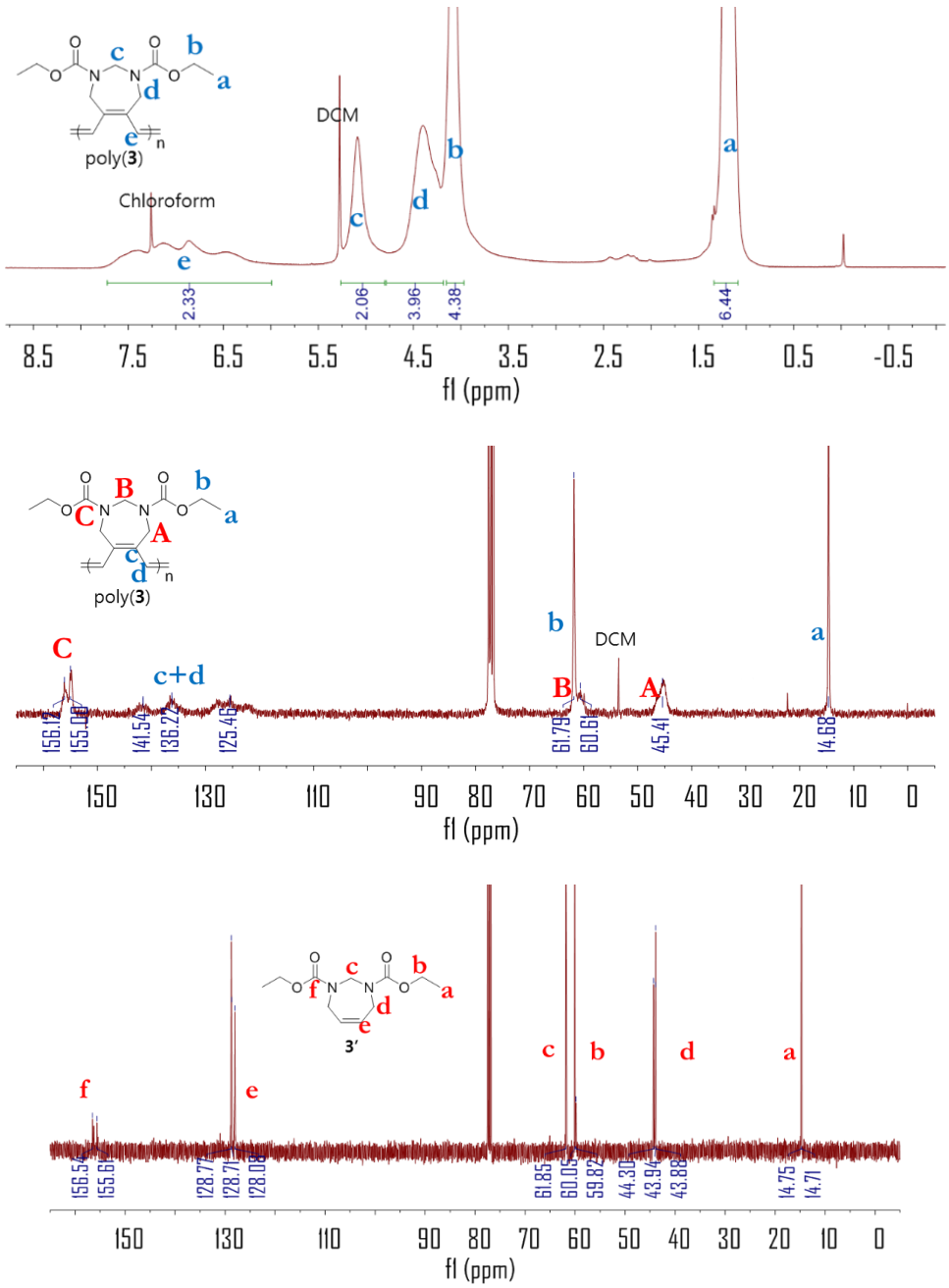


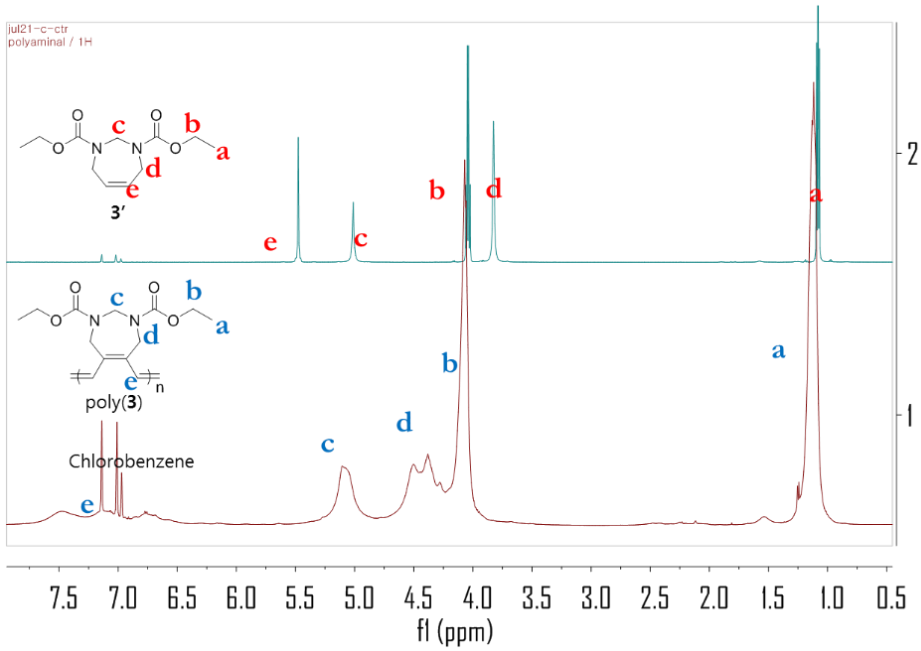
Figure S8. ^{1}H and ^{13}C NMR Spectra of Polymers

Broad signals in ^{1}H NMR and multiple signals in ^{13}C NMR spectra of aminal polymers are due to rotamers thus, we took NMR at high temperature (exact temperature is stated in each NMR spectrum).

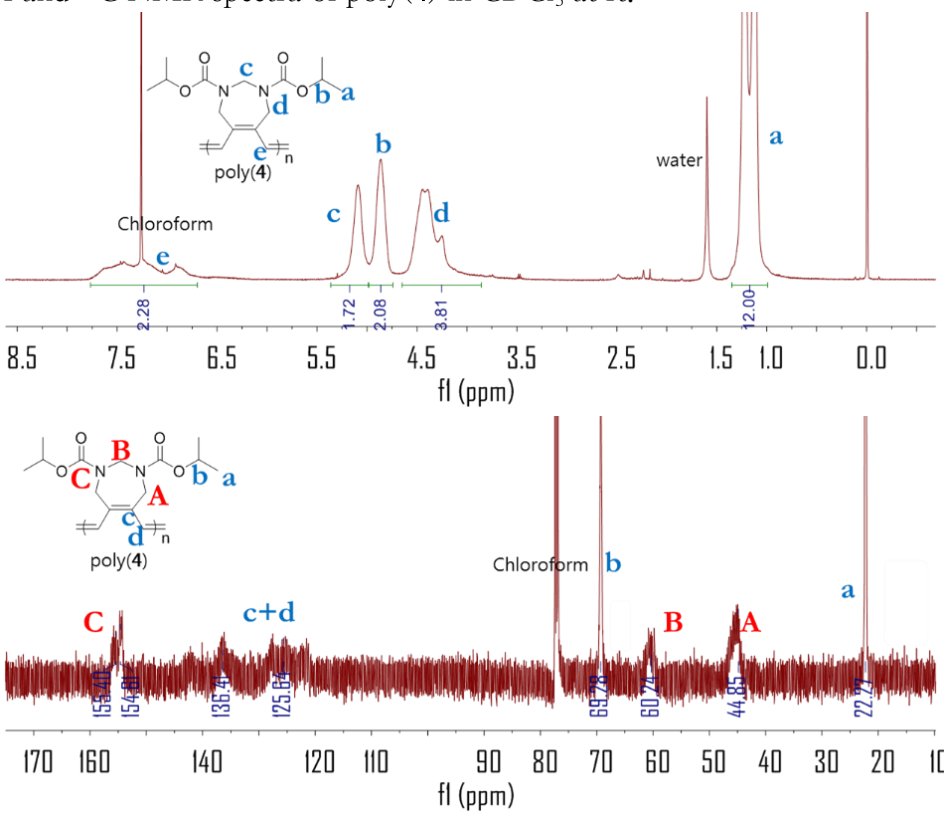
^{1}H and ^{13}C NMR spectra of poly(**3**) and **3'** in $CDCl_3$ at rt.



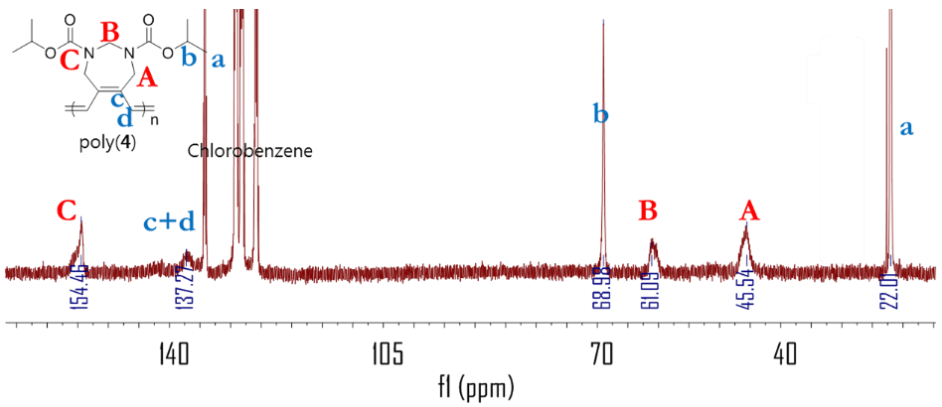
^{1}H NMR spectra of **3'** and poly(**3**) in chlorobenzene-d_5 at 90 ℃.



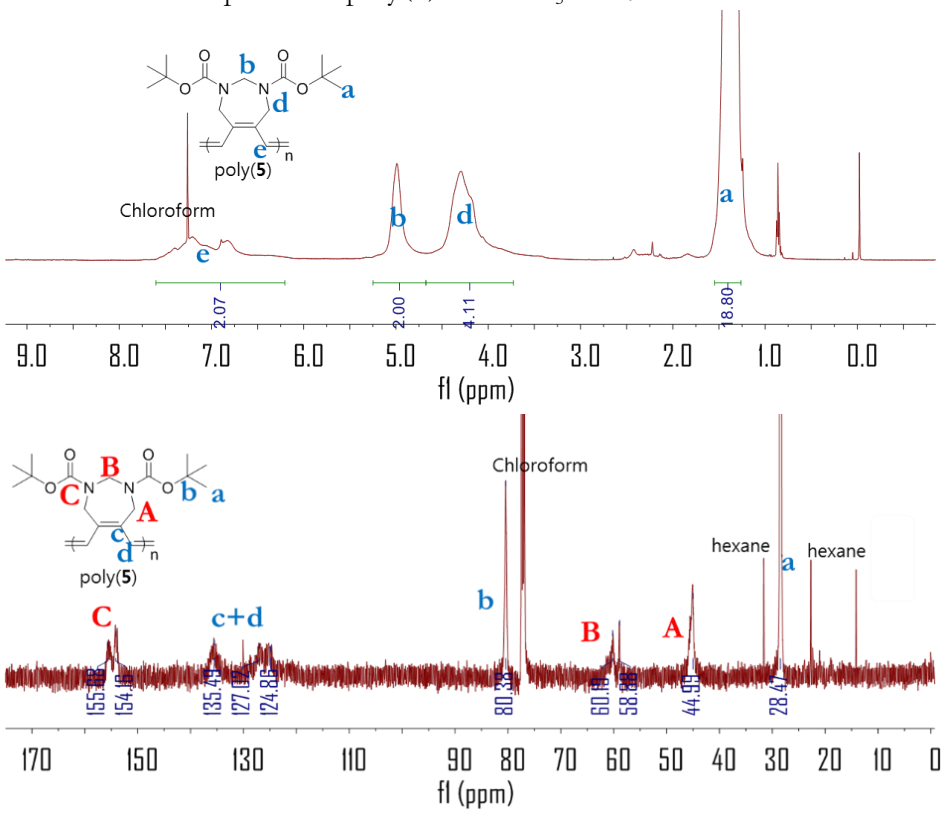
^{1}H and ^{13}C NMR spectra of poly(**4**) in $CDCl_3$ at rt.



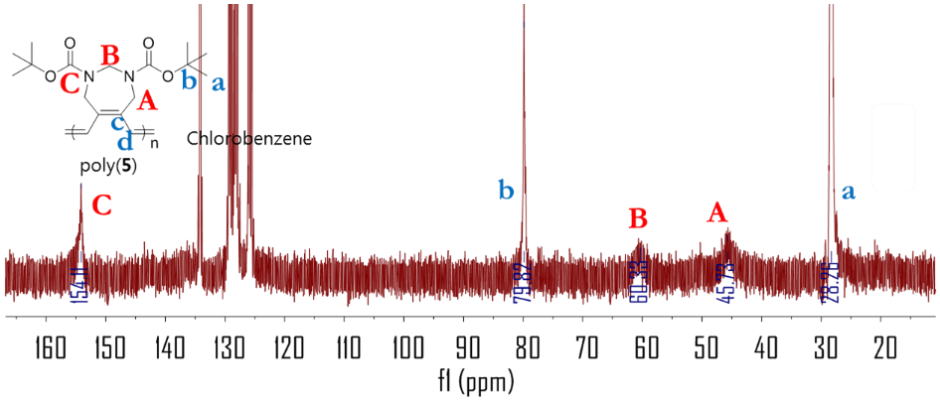
^{13}C NMR spectrum of poly(**4**) in chlorobenzene-d_5 at 70 ℃.



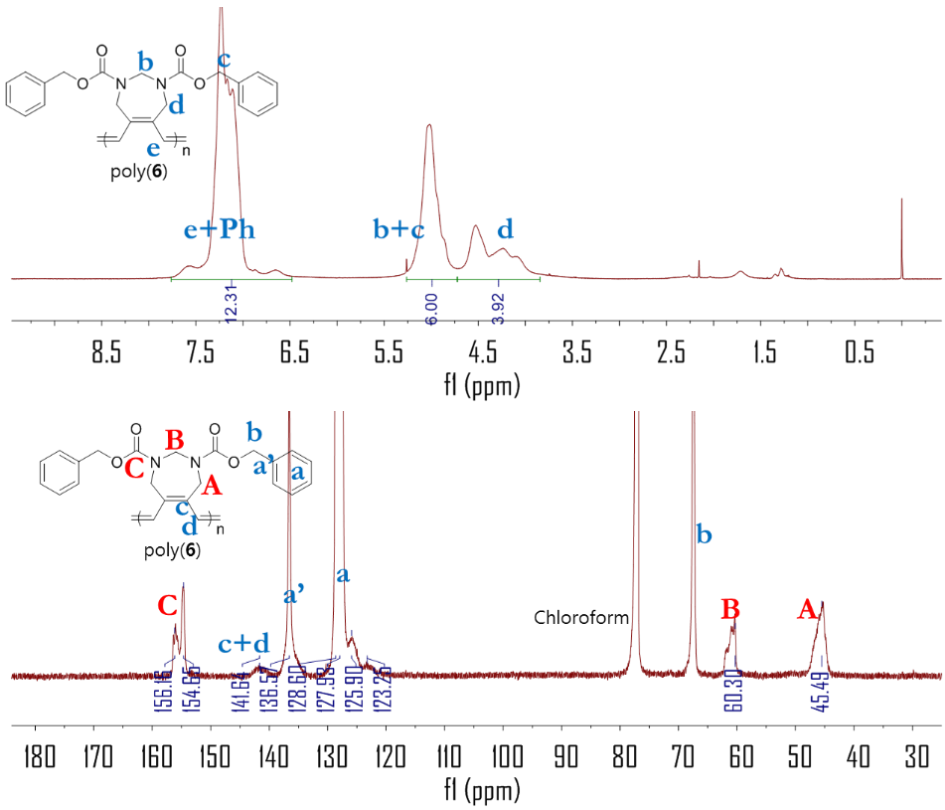
^{1}H and ^{13}C NMR spectra of poly(**5**) in $CDCl_3$ at rt.



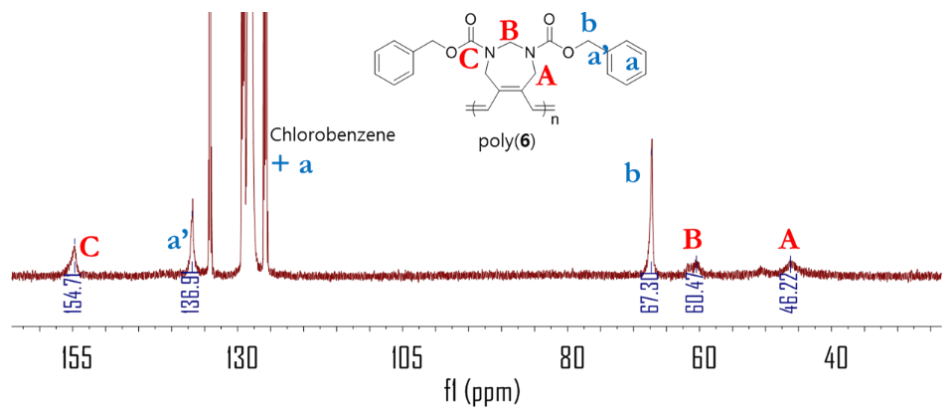
^{13}C NMR spectrum of poly(**5**) in chlorobenzene-d_5 at 80 ℃.



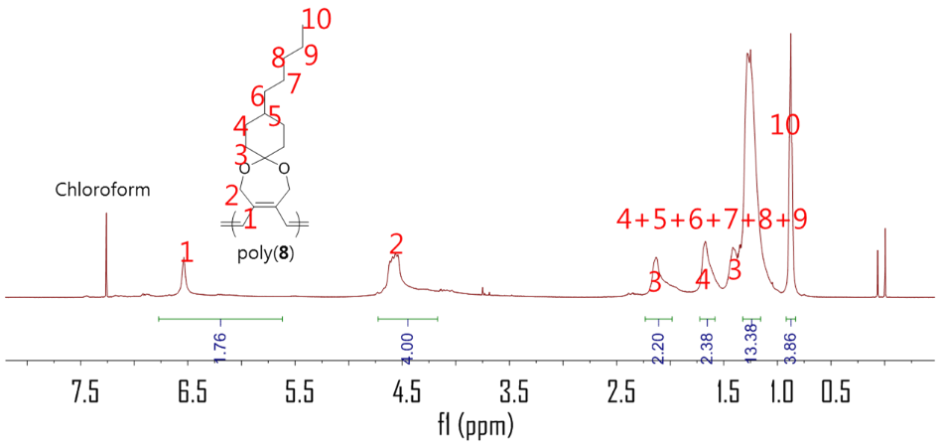
^{1}H and ^{13}C NMR spectra of poly(**6**) in $CDCl_3$ at rt.



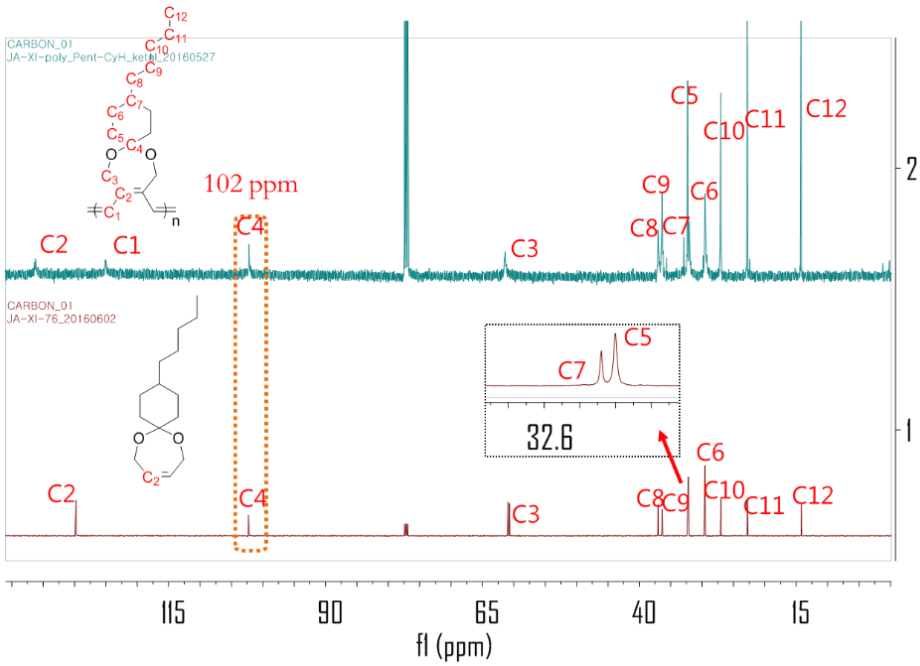
^{13}C NMR spectrum of poly(**6**) in chlorobenzene-d_5 at 70 ℃.



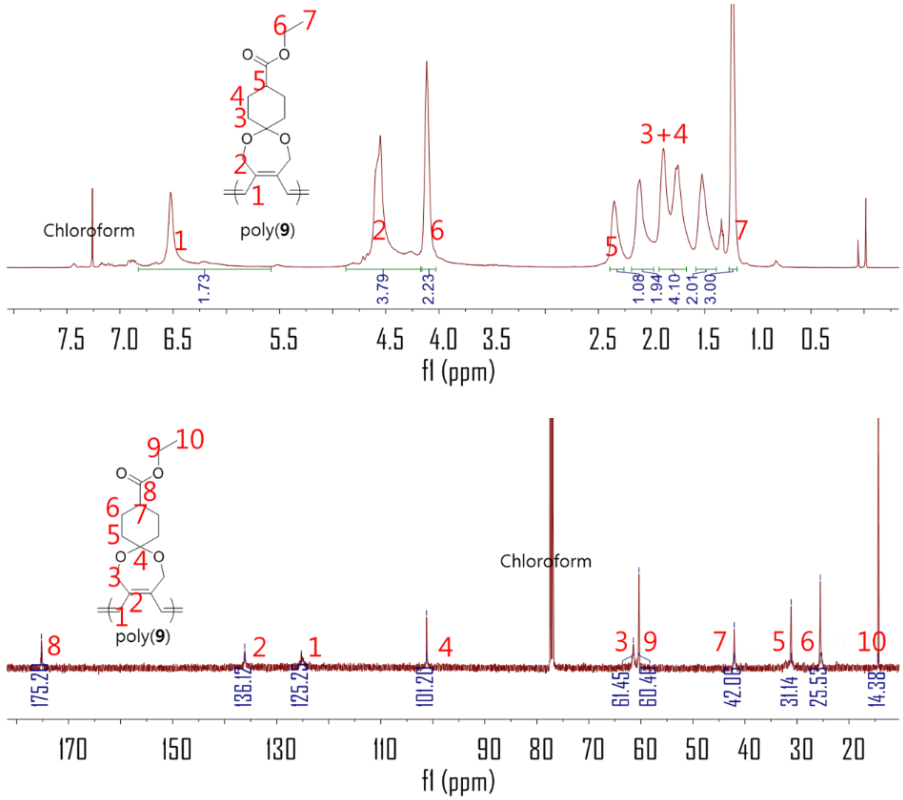
^{1}H NMR spectra of poly(**8**) in $CDCl_3$ at rt.



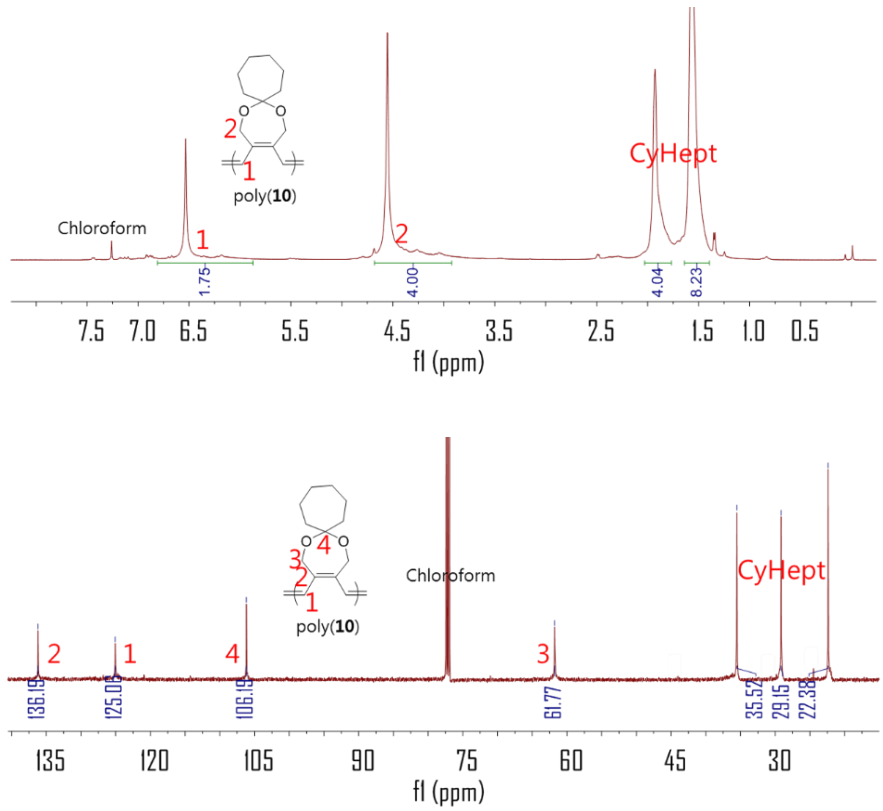
^{13}C NMR spectra of poly(**8**) and **8'** in $CDCl_3$ at rt.



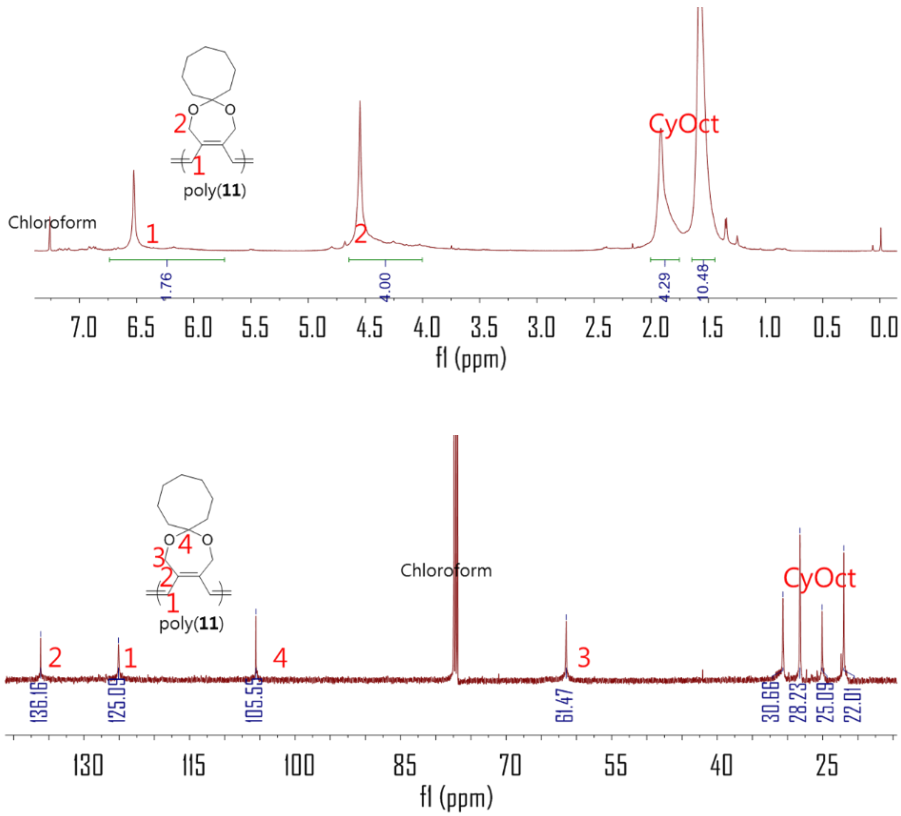
^{1}H and ^{13}C NMR spectra of poly(**9**) in $CDCl_3$ at rt. Single quaternary carbon signal was observed at 101.20 ppm.



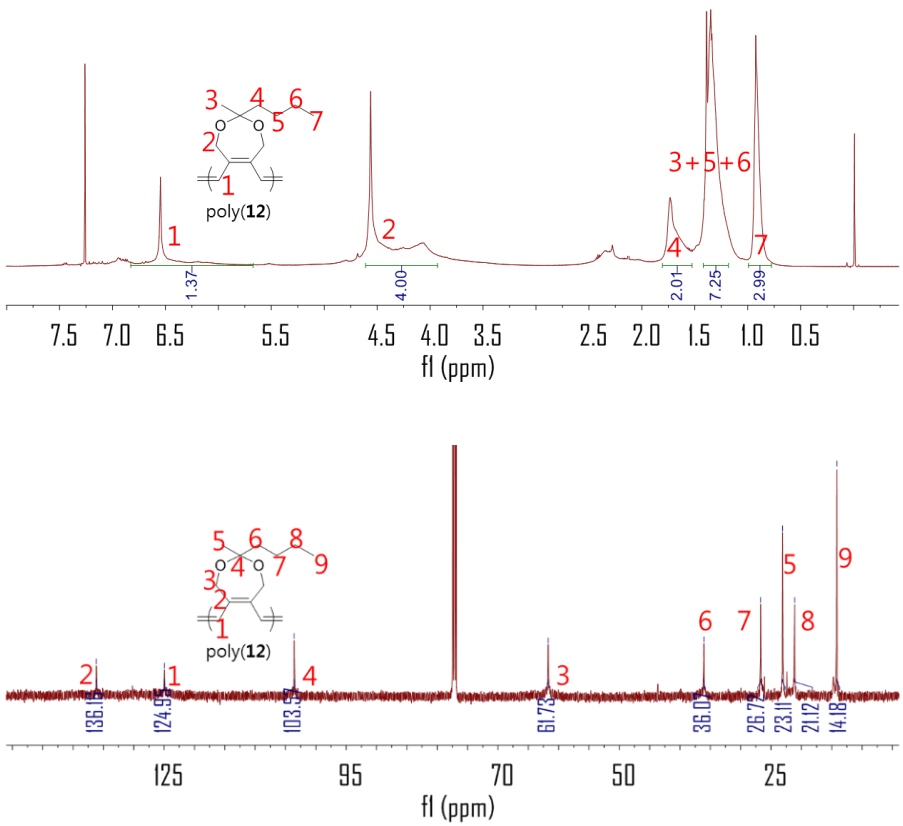
^{1}H and ^{13}C NMR spectra of poly(**10**) in $CDCl_3$ at rt. Single quaternary carbon signal was observed at 106.19 ppm.



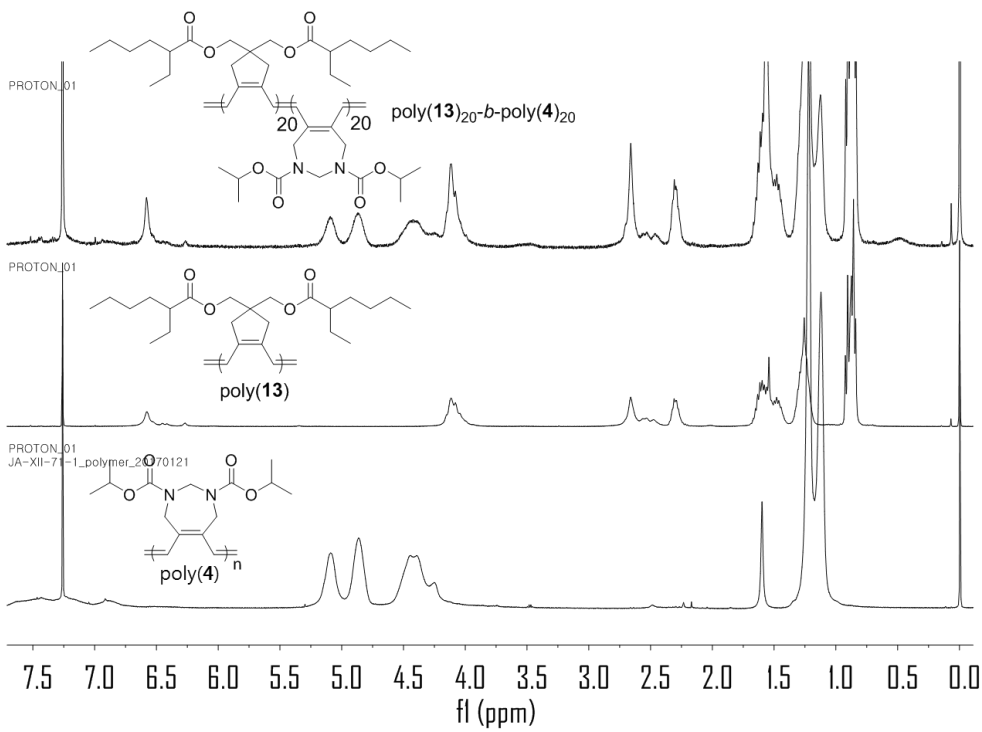
^{1}H and ^{13}C NMR spectra of poly(**11**) in $CDCl_3$ at rt. Single quaternary carbon signal was observed at 105.55 ppm.



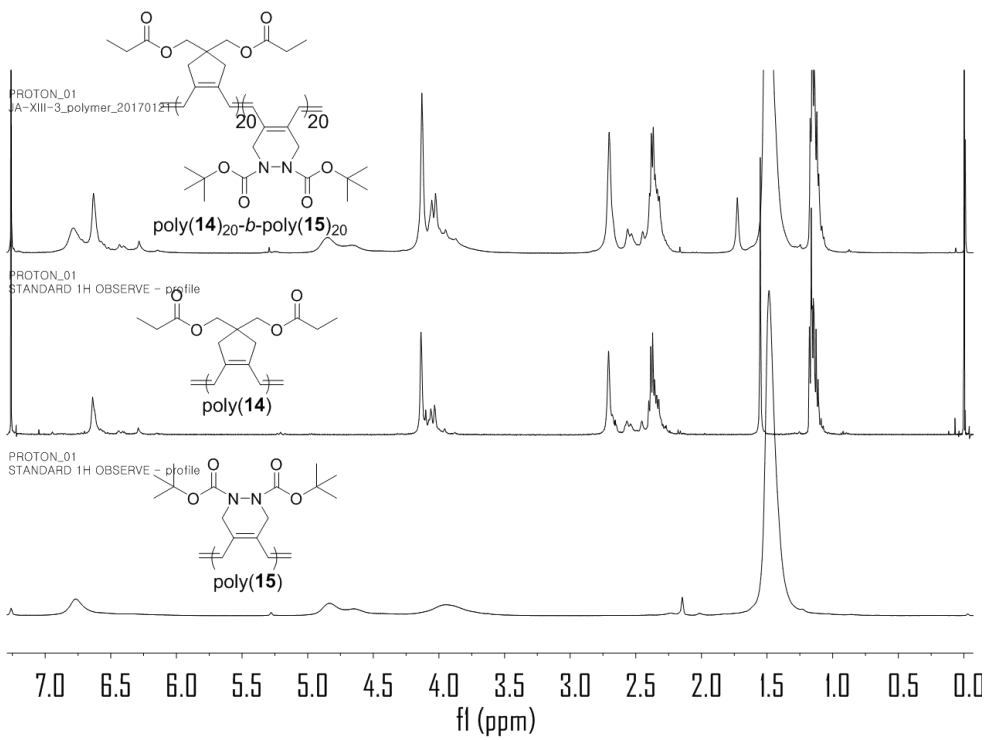
^{1}H and ^{13}C NMR spectra of poly(**12**) in $CDCl_3$ at rt. Single quaternary carbon signal was observed at 103.57 ppm.



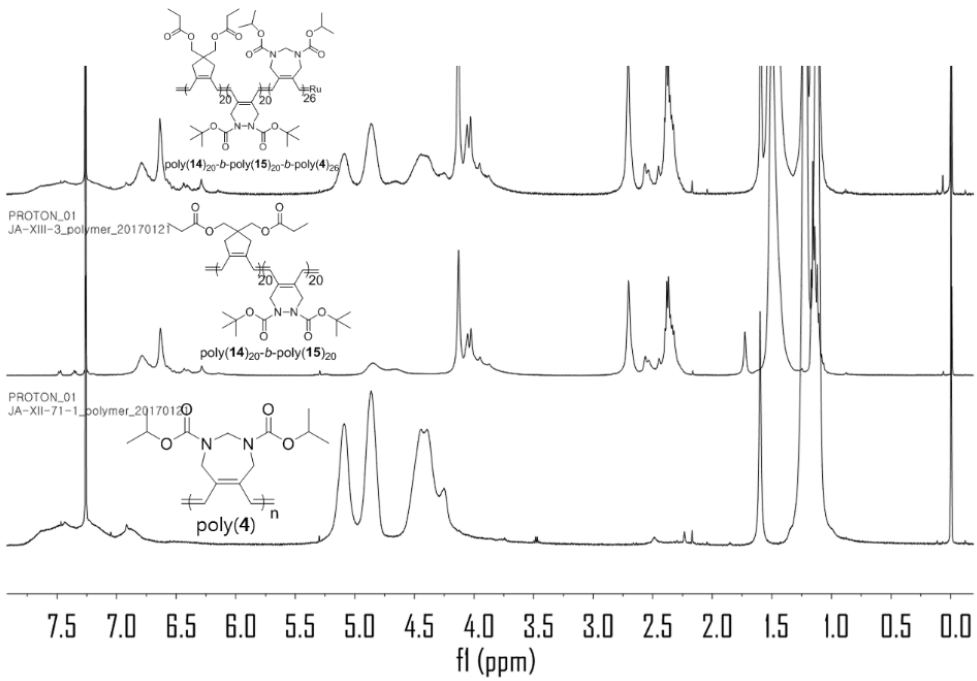
^{1}H NMR spectra of poly(**13**)$_{20}$–*b*–poly(**4**)$_{20,}$ poly(**13**) and poly(**4**) in $CDCl_3$ at rt.



^{1}H NMR spectra of poly(**14**)$_{20}$–*b*–poly(**15**)$_{20,}$ poly(**14**) and poly(**15**) in $CDCl_3$ at rt.



^{1}H NMR spectra of poly(**14**)$_{20}$–*b*–poly(**15**)$_{20}$–*b*–poly(**4**)$_{26}$, poly(**14**)$_{20}$–*b*–poly(**15**)$_{20}$ and poly(**4**).



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Chapter 4 Controlled ROMP of *cis*–cyclooctene

4.1 Abstract

In this section, we will discuss controlled ring-opening metathesis polymerization of 3-substituted cyclooctene using Grubbs 3rd generation catalyst. To hinder chain-transfer reaction, we introduced bulky substituents and ring-opening metathesis polymerization of OTIPS substituted cyclooctene was controlled. However, this was limited to high livingness.

4.2 Introduction

Ring-opening metathesis polymerization (ROMP) of cyclooctene (COE) or cyclooctadiene (COD) gives various polyalkenamers, which have broad potential in a variety of fields because they have low glass transition temperature and yield High Density Polyethylene (HDPE) upon hydrogenation.[1] First ROMP of cyclooctene using $WCl_6/AlEt_3$ was reported by Natta in 1966.[2] Then, Katz first used well-defined catalyst for ROMP of COE giving 97% *cis* olefin-containing polyalkenamer.[3] With the development of W-based Schrock catalysts, controlled ROMP of COE and COD was possible.[4,] Use of Ru-based Grubbs catalyst for ROMP of COE and COD was also reported.[5,1] Furthermore, highly active and functional group tolerant Schrock and Grubbs catalysts polymerized substituted COEs, then it caused

regioselectivity issue (head-to-tail, head-to-head and tail-to-tail). Hillmyer group successfully obtained highly regioselective head-to-tail polymers, which was possible due to steric repulsion between NHC ligand and substituents at C3 position (Figure 4.1).[6] However, living ROMP of COE and COD was challenging due to low ring-strain (7.4 kcal/mol) and secondary metathesis. The strategy of Grubbs group to overcome this problem was the utilization of more strained *trans*-cyclooctene (16.7 kcal/mol) and it was successful for living ROMP.[7] In this section, we discuss the strategy for controlled ROMP of *cis*-Cyclooctene: introduction of bulky substituent and two substituents at C3 position to hinder chain transfer reaction and increase ring strain.

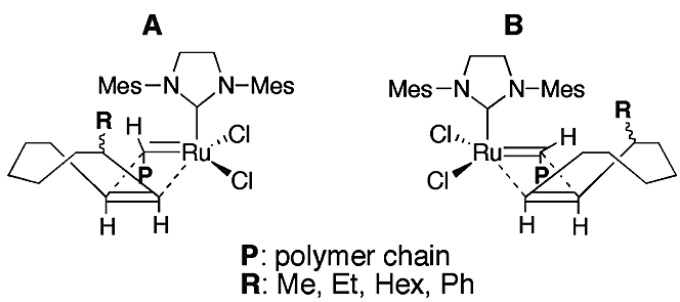
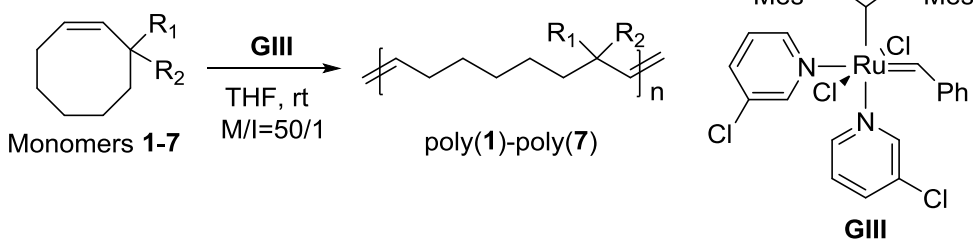


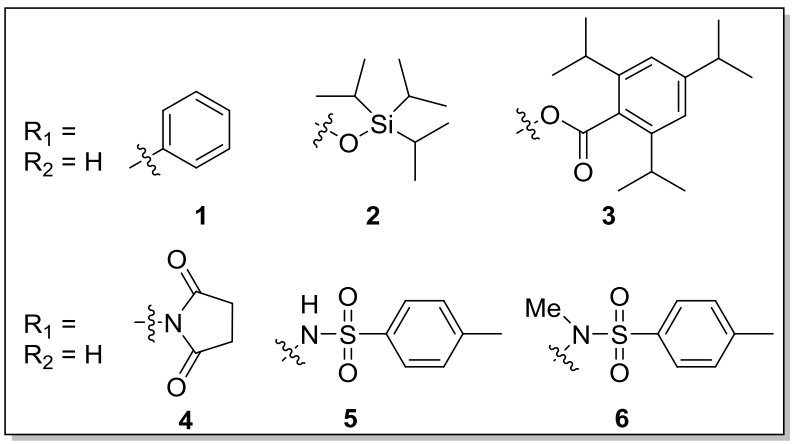
Figure 4.1 Orientation during ROMP of 3-substituted COEs[6]

4.3 Results and Discussion

As our initial attempt, 3-substituted cyclooctene **1**, which showed narrow PDI in the ROMP using **GII**[6], was polymerized this using fast-initiating third generation Grubbs catalyst (**GIII**)[8]. This reaction gave broad PDI over than 1.4 even at conversion 84% presumably because chain transfer reaction occurred due to small phenyl group (Table 4.1, entry 1). To hinder chain transfer reaction, we prepared monomers having bulkier substituents and heteroatom-bridge to shorten the distance between substituent and olefin (**2**-**6**). Treating the ether-containing monomer **2** with 2 mol% **GIII** gave the desired polymer (M_n of 20 kDa) with narrow PDI of 1.25 (Table 4.1, entry 2). Ester-containing monomer **3** was converted to the corresponding polymer (M_n of 27 kDa) in 15 min with somewhat narrow PDI of 1.34 (Table 4.1, entry 3). Next, ROMP of imide-containing monomer **4** in higher concentration (1.8 M) to accelerate the rate gave the polymer (M_n of 17 kDa) with narrow PDI of 1.53 at conversion 90% (Table 4.1, entry 4). Sulfonylamide-containing monomer **5** was successfully polymerized but yielded insoluble polymer because of hydrogen bonding (Table 4.1, entry 5). To eliminate the hydrogen bonding, methyl group was introduced (**6**) and ROMP of this monomer gave soluble polymer (M_n of 27.2 kDa) with narrow

Table 4.1 ROMP of Monomers 1–7



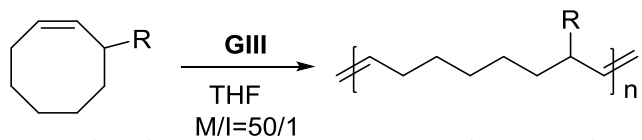


Entry	Monomer	Conc. (M)	Time (h)	M_n (kDa)[a]	PDI[a]	Conv. (%)[b]	Yield (%)[c]
1[d]	1	0.8	1	16	1.42	84	62
2	2	1.0	1	20	1.25	96	92
3	3	1.0	0.25	27	1.34	100	89
4	4	1.8	1	17	1.53	90	77
5	5	1.0	1	insoluble		100	65
6	6	1.0	1	27.2	1.37	84	54

[a] Determined by THF SEC calibrated using polystyrene (PS) standards. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yield after purification. [d] M/I is 25/1.

PDI of 1.37 at conversion 84% (Table 4.1, entry 6). In short, as our expectation, bulkier group and heteroatom-bridge were not critical but effective to give narrower PDIs. Obtained polymers were characterized by ^{1}H NMR analysis. The polymers exhibited only two olefinic signals, revealing perfect *trans*-head-to-tail.

Table 4.2 Optimization of Conditions for ROMP of **3** and **6**.



Monomers **3** or **6** poly(**3**) or poly(**6**)

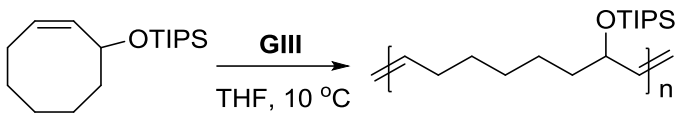
Entry	Monomer	Temp. (℃)	Conc. (M)	Time (h)	M_n (kDa)[a]	PDI[a]	Conv. (%)[b]	Yield (%)[c]
1	**3**	10	1.0	0.5	18.7	1.20	50	46
2	**3**	0	1.0	3	26.2	1.30	88	71
3	**6**	10	1.5	2	16.7	1.25	42	17
4	**6**	0	1.0	8	12.4	1.37	27	12

[a] Determined by THF SEC calibrated using polystyrene (PS) standards. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yield after purification.

For controlled polymerization, we lowered the reaction temperature to stabilize the propagating carbene.[9] For monomer **3**, lower temperature 10 ℃ were tested but the polymer (M_n of 18.7 kDa) with PDI of 1.20 was obtained even at conversion 50%. (Table 4.2, entry 1). We further lowered the

temperature up to 0 ℃ but PDI reached to 1.30 before complete conversion (Table 4.2, entry 2). For monomer **6**, both reaction temperatures of 10 and 0 ℃ decreased the reactivity and yielded the corresponding polymers with PDI of 1.25 and 1.37, respectively before reaching 50% conversion (Table 4.2, entries 3 and 4).

Table 4.3 Controlled ROMP of **2**.



Entry	M/I	Conc. (M)	Time (h)	M_n (kDa)[a]	PDI[a]	Conv. (%)[b]	Yield (%)[c]
1	50/1	1.0	4	20	1.22	93	49
2	50/1	1.5	3	19	1.18	100	43
3	75/1	1.8	6	35	1.33	100	77
4	100/1	1.5	9	62	1.46	100	87

[a] Determined by THF SEC calibrated using polystyrene (PS) standards. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yield after purification.

Thus, more reactive monomer **2** was next polymerized at 10 ℃. The desired polymer (M_n of 20 kDa) was obtained with PDI of 1.22 at 93% conversion (Table 4.3, entry 1). To accelerate the reaction, we increased concentration from 1.0 M to 1.5 M and the complete conversion was observed in 3 h, yielding the polymer with narrow PDI of 1.18 (Table 4.3, entry 2). Then, at

10 ℃, controlled ROMP of **2** was attempted. Fortunately, molecular weights of poly(**2**) were directly proportional to the M/I (from 19 kDa to 62 kDa with M/I from 50/1 to 100/1) and their PDIs were fairly narrow (Table 4.3, entries 2–4 and Figure 4.4). Although we could achieve controlled ROMP of **2**, higher ring-strain was required for higher controllability.

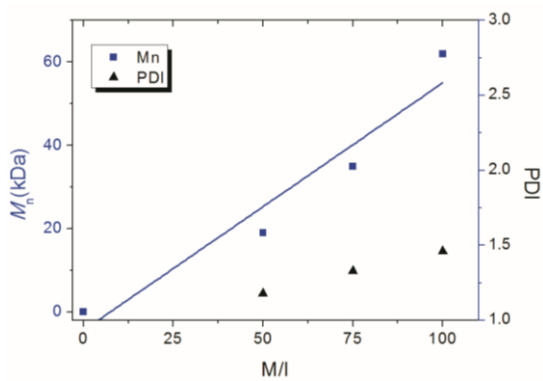
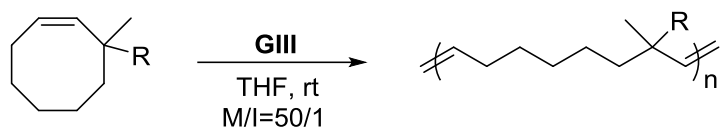


Figure 4.4 (a) Plots of Mn vs. M/I and corresponding PDI values for poly(**2**) and (b) their SEC traces

To further increase the controllability, we designed a 3,3-disubstituted *cis*-cyclooctene **7** because we expected that **7** would have higher ring strain than mono-substituted one like the case of cyclopentene or cyclohexene whose disubstituted derivative has higher ring strain than non-substituted one. However, ROMP of **7** didn't give any polymeric product (Table 4.4, entry 1). To confirm whether the origin of failure is due to lower ring strain or steric

hindrance, we carried out ROMP of **8** having hydroxyl group instead of trimethylsilyl (TMS) protecting group and **8** didn't convert to the corresponding polymer at all (Table 4.4, entry 2). Therefore, 3,3-disubstituted *cis*-cyclooctene was not a proper monomer for ROMP due low ring strain.

Table 4.4 ROMP of 3,3-disubstituted monomer **7** and **8**



7: R = OTMS
8: R = OH

Entry	Monomer	Conc. (M)	Conv. (%)
1	**7**	1.0	0
2	**8**	1.5	0

4.4 Conclusion

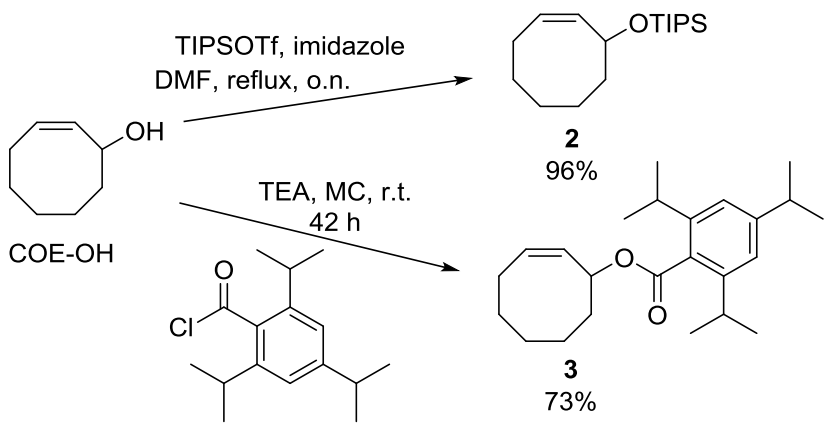
In conclusion, we achieved controlled ROMP of 3-substituted *cis*-cyclooctene by introduction of bulky substituent OTIPS to hinder chain transfer reaction. However, intrinsic low reactivity of *cis*-cyclooctene due to low ring strain limited high controllability for ROMP of *cis*-cyclooctene.

4.5 Experimental

General procedure for cyclopolymerization: Monomer (0.1 mmol) was

weighed in a 4-ml sized screw-cap vial with septum and purged with argon. Anhydrous and degassed solvent was added to the vial. The solution of initiator was added at once under vigorous stirring. After confirming the monomer conversion by TLC, the reaction was quenched by excess amount of ethyl vinyl ether. The concentrated mixture was precipitated by methanol or hexane. The obtained polymer was dried *in vacuo*.

Monomer **1**, COE-Br and COE-OH were prepared according to the literature.[6]

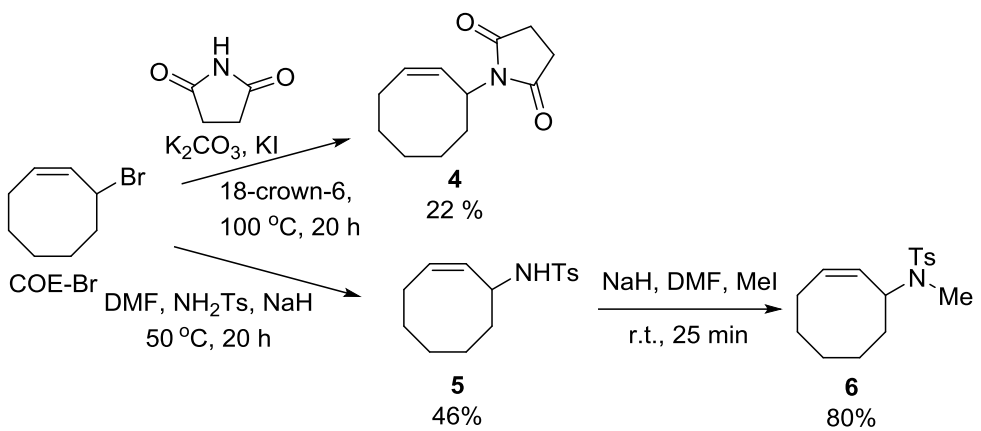


Scheme S4.1 Synthesis of Monomers **2** and **3**

2: TIPSOTf (0.5 ml, 1.90 mmol) and imidazole (0.13 g, 1.90 mmol) were added to the solution of COE-OH (0.2 g, 1.58 mmol) in DMF (5.3 ml) under stirring. The solution was refluxed overnight. After quenching with water, the product was extracted with diethyl ether and was washed with brine. The

organic layer was dried with $MgSO_4$ and concentrated. The product was purified by column chromatography (Hexane) to afford the product **2** (0.43g, 1.52 mmol, 96% yield).

3: 2,4,6-Triisopropylbenzoyl chloride (0.51 g, 1.90 mmol) and TEA (0.27 ml, 1.90 mmol) were added to the COE-OH (0.2 g, 1.58 mmol) solution in DCM (5.3 ml) under stirring. The solution was stirred for 42 h. After quenching with water, the product was extracted with DCM and washed with brine. The organic layer was dried with $MgSO_4$ and concentrated. The product was purified by column chromatography to afford the product **3** (0.41 g, 1.15 mmol, 73% yield).



Scheme S4.2 Synthesis of Amide Monomers **4**-**6**

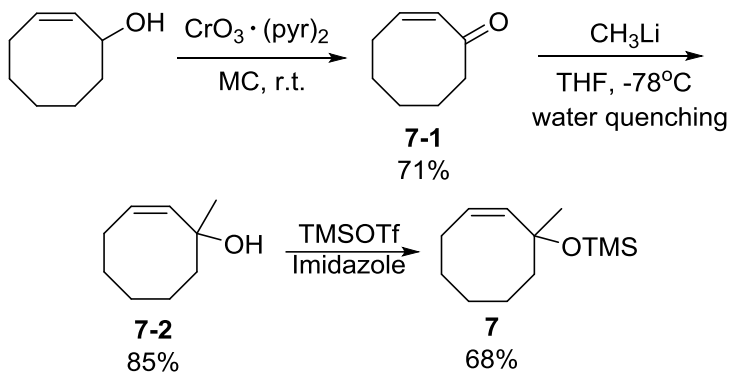
4: K_2CO_3 (0.33 g, 2.42 mmol) were added to the succinimide (0.2 g, 2.02 mmol) solution in DMF (6 ml) and the reaction mixture was stirred for 15

min. COE-Br (0.46 g, 2.42 mmol), 18-crown-6 (53 mg, 0.20 mmol) and KI (33 mg, 0.20 mmol) were added to the reaction mixture, which then stirred for 20 h at 100 ℃. The reaction mixture was cooled down to room temperature and quenched with water. The product was extracted with diethyl ether and washed with brine. The organic layer was dried over $MgSO_4$ and concentrated. The product was purified by column chromatography to afford **4** (92.1 mg, 0.44 mmol, 22% yield).

5: NaH (56 mg, 1.40 mmol) was added to tosyl amide (0.2 g, 1.17 mmol) solution in DMF (4 ml) and the reaction mixture was stirred at rt for 15 min. Then, COE-Br (0.27 g, 1.40 mmol) was added to the solution and the reaction mixture was stirred at 50 ℃. After 20 h, the reaction was cooled down to room temperature and quenched with water. The product was extracted with diethyl ether and washed with brine. The product was extracted with diethyl ether and washed with brine. The organic layer was dried over $MgSO_4$ and concentrated. The product was purified by column chromatography to afford **5** (0.15 g, 0.54 mmol, 46% yield).

6: NaH (10.4 mg, 0.43 mmol) was added to the DMF (1.2 ml) solution of **5** (0.1 g, 0.36 mmol) and the reaction mixture was stirred for 15 min. MeI (34 μl, 0.54 mmol) was added to the reaction mixture, which then stirred for 25

min. The reaction was quenched with water and the product was extracted with diethyl ether and washed with brine. The organic layer was dried over $MgSO_4$ and concentrated. The product was purified by column chromatography to afford **6** (85 mg, 0.29 mmol, 80%).



Scheme S4.3 Synthesis of Amide Monomers **7**

7-1: $CrO_3(pyr)_2$ (2.74 g, 12.7 mmol) was added to DCM (32 ml) solution of COE-OH (0.4 g, 3.16 mmol). The reaction mixture was stirred overnight and the reaction was filtered through a pad of Celite. The solution was concentrated and purified by column chromatography to afford the **7-1** (0.28 g, 2.24 mmol, 71% yield).

7-2: MeLi (1.4 ml, 1.6 M in ether) was added to THF solution of **7-1** (0.28g, 2.24 mmol) at −78 ℃. The reaction mixture was stirred for 2 h at −78 ℃. Water was added to the reaction mixture and slowly heated up to room temperature. The product was extracted with DCM, dried over $MgSO_4$ and

concentrated. The product was purified by column chromatography to afford **7-2** (0.27 g, 1.90 mmol, 85%).

7: TMSOTf (0.5 ml, 1.90 mmol) and imidazole (0.13 g, 1.90 mmol) were added to DMF solution of **7-2** (0.2 g, 1.43 mmol). The reaction was stirred overnight and quenched with water. The product was extracted with diethyl ether, washed $MgSO_4$ and concentrated. The product was purified by column chromatography to afford **7** (0.21 g, 0.97 mmol, 68%).

4.6 References

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